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THE DETERMINATION OF HEAVY WATER¹

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Abstract

A reasonably simple procedure for determining the concentration of heavy water solutions, based on the comparison of the vapor pressures of these solutions with pure water, has been developed. The method is useful for samples as small as 0.5 mgm. and the sample may be recovered. Individual determinations require about two hours. In the work reported, mean determinations did not vary from the best curve through the experimental points by more than 0.2 mole % of D₂O, while the spread in any group of readings was about ± 0.25 mole %.

Introduction

Various methods have been proposed for the determination of the concentration of heavy water solutions. Procedures based on the measurement of vapor pressures of the solutions do not appear to have been employed, however. The recent development of a simple mercury manometer, capable of high sensitivity, made this method seem feasible since the published values for pure D₂O indicate a vapor pressure difference from pure water of approximately 0.03 mm. for each mole per cent of D₂O present in solution at 20°C. This communication presents experimental results that show that the method is not only feasible but should constitute a useful analytical tool.

Experimental

The apparatus, shown in Fig. 1, is built around the differential manometer. Although this manometer has been described elsewhere (2) a short description will be repeated here to clarify the experimental procedure.

The short, wide cylinders *A* and *B* form the arms of a U-tube. These are connected with 3 mm. capillary through a stopcock at *C*. The bulb at *D*, which has about one-half the volume of *B*, is connected to *B* with a length of capillary selected for uniformity of bore. The sections of 1 mm. capillary above *B* and *D* are etched at *F* and *G*.

The manometer is operated as follows. Sufficient clean mercury is admitted through *H* to the evacuated assembly, and the end of the thread adjusted to *G*. Stopcock *C* is left open and the three-way tap at *J* turned to connect the spaces

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above the mercury in *A* and *B*. The mercury in these two cylinders should now be at the same level. Stopcock *C* is then closed and air admitted through a slow leak at *I*; this forces the mercury from *D* into *B* filling it to *F*. The

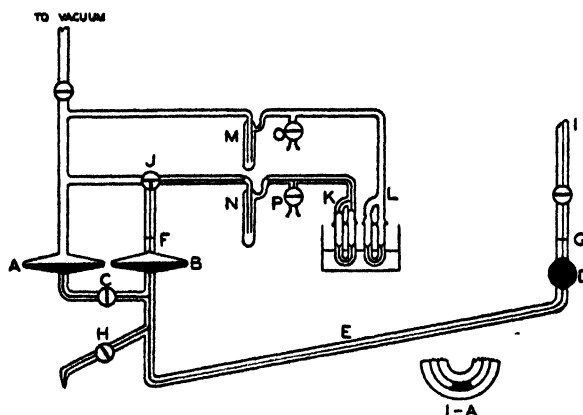


FIG. 1. *Apparatus.*

volume of mercury in the apparatus should be such that on adjustment of its level at *F* the other end of the thread should be near the lower end of the capillary *E*. This point on *E* represents the zero reading of the manometer. The mercury is now returned to *G*, stopcock *C* opened and *J* turned to connect *B* with *K*. If the sample holders *K* and *L* contain liquids that differ slightly in vapor pressure, with that in *L* being the higher, mercury will flow from *A* to *B* until equilibrium is established. If *C* is now closed and the procedure for finding the zero point repeated, the volume of mercury that flowed from *A* to *B* will be represented by the increased length of the mercury thread in *E*. The pressure difference may then be calculated from the known geometry of the apparatus.

It is obvious that *A* and *B* must be mounted rigidly with respect to each other. In the present work they were cast in a block of plaster of Paris, which was supported on a stand of four 1/2 in. rods clamped to each other and secured to the bench with floor flanges. Stopcock *C* was supported on the same frame.

The cylinders *A* and *B* were made from 46 mm. I.D. Pyrex tubing while *E* had a diameter of 0.78 mm. This gives a theoretical magnification of pressure differences of 1740. Actually, the diameter of one of the cylinders was slightly reduced in forming the cylinder, and the magnification factor found on calibration with a McLeod gauge, using air as the working substance, was 1650, that is, 1 mm. on the *E* scale was equivalent to a pressure difference of 0.000606 mm. Cylinder *B* had a volume of 23 cc. and the inner side walls of both *A* and *B* were etched with carborundum powder prior to assembly.

The sample holders *K* and *L* were made in the form of U's and were attached to the tubes connected with the manometer arms with standard taper ground

glass joints. The curved portions of these holders, which actually contained the samples, were made from 0.5 mm. capillary. Samples condensed here in slugs of the form shown in Fig. 1-A. This procedure ensured surfaces of equal curvature, and any error due to the high vapor pressure of small droplets was avoided. No difficulty was experienced in the bridging of the condensed droplets to form slugs, provided the capillaries were kept clean, and this could be done readily by periodic, thorough steaming. The capillary portions were almost completely immersed in the thermostat liquid.

Test samples of heavy water were made up gravimetrically from a sample of known concentration and water that had been purified by distillation from alkaline permanganate. Amounts of 1 to 2 mgm. were drawn up into short pieces of 0.5 mm. capillary placed in a small container, and attached to the apparatus at *P*. A similar sample of pure distilled water was connected at *O*. These samples were then admitted to the evacuated apparatus and trapped at *M* and *N* using dry ice as a refrigerant. Dissolved air was removed by several cycles of condensation and evaporation, the system being pumped down to a "click" vacuum on a McLeod gauge with each condensation. When free from air, the samples were condensed into the capillaries of the sample holders, and readings of the pressure difference taken after equilibrium was established. The thermostat was held at $20 \pm 0.01^\circ \text{C}$.

About six readings of the pressure difference were taken for each sample, the zero point being checked after each reading. This procedure is desirable, since changes in room temperature will change the zero reading of the manometer. The zero point could be checked without dilution of the D_2O solution by forcing the mercury nearly to *J* in the capillary above *B* before the three-way stopcock was turned to connect *A* with *B*. A similar procedure was followed before connecting *B* with *K* once again. Equilibrium was established rapidly and it was quite possible to take readings every 15 min.

Although samples of not less than 1 mgm. were used in the present work, it seems quite probable that these could be reduced to 0.5 mgm. by reducing the dead space. The volume of *B* may be made as small as 14 cc. without sacrificing the 46 mm. diameter. By making the trap *N* small and using large diameter capillary for connecting tubing, about 0.3 mgm. of vapor at 20°C . should fill the dead space, leaving a slug of liquid about 1 mm. long in the sample holder. Very little fractionation of the sample takes place and the use of such small samples seems to be quite feasible.

Some idea of the precision of the method can be obtained from the following set of *E* scale readings obtained for one sample. These figures were selected at random and are representative of the reproducibility obtainable: 219, 224, 213, 216, 203, 214. Examination of Fig. 2 shows that these figures correspond to a total spread of 4.75 to 5.25 mole % of D_2O .

The experimental values for the vapor pressure lowerings, using the micro samples, are given in Table I.

TABLE I
EXPERIMENTAL VALUES OF VAPOR PRESSURE LOWERING

Mole % D ₂ O	Mean <i>E</i> scale reading, mm.	ΔP , mm.
1.42	60	0.036
3.38	145	.088
4.86	215	.130
9.89	438	.265
13.15	575	.348

These values, together with results obtained when large samples (0.5 cc.) were used, are shown graphically in Fig. 2. With the large samples, bulbs equipped with magnetic stirring devices were used as sample holders. The

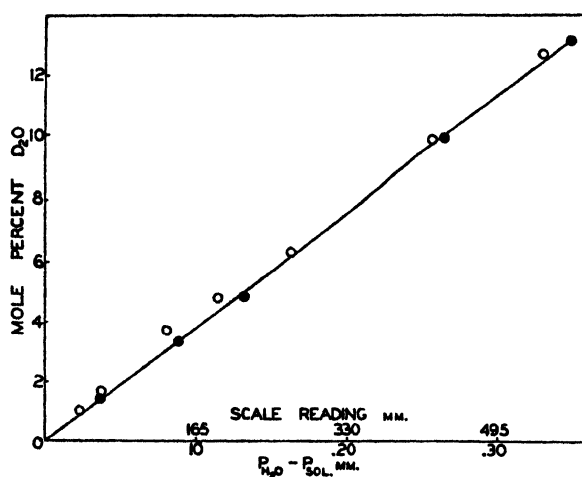


FIG. 2. Lowering of the vapor pressure with increased D₂O concentration. Open circles, values obtained with 0.5 gm. samples; filled circles, values obtained with micro samples.

data from the large samples are more erratic than those from the micro samples. They show, however, that fractionation of the sample during a determination is not serious since in no instance do they deviate from the micro samples by more than 0.5%. None of the mean values for the micro samples depart from the best curve drawn through the points by more than 0.2%. The microtechnique has the added advantage of requiring much less time for degassing the sample.

Since H₂O and D₂O might be expected to form an ideal solution and obey Raoult's law, a reasonable value for $P_{H_2O} - P_{D_2O}$ should be obtained by extrapolating the curve in Fig. 2 to 100 mole % of D₂O. The value found doing this is 2.62 mm. This is probably slightly high owing to sample

fractionation. Extrapolation of the best curve through the points obtained with 0.5 gm. samples indicates a value of 2.47 mm., which is in good agreement with the value of 2.48 mm. given by Miles and Menzies (1).

Measurements of ΔP at concentrations higher than 14 mole % of D_2O were not attempted, since the total range of the manometer used in the work was only 0.4 mm. The work done, however, indicates the usefulness of the method and probably covers the range that will be encountered most frequently. Higher concentrations could, of course, be determined by suitably diluting the sample.

Although no specific examples can be cited, it is suggested that this approach might be of use in determining the composition of other two-component systems.

Acknowledgment

Grateful acknowledgment is made to Dr. E. W. R. Steacie who suggested the problem.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXX. DETERMINATION OF THE FERMENTATION ACIDS BY PARTITION CHROMATOGRAPHY¹

By A. C. NEISH²

Abstract

A procedure has been developed for the estimation of butyric, acetic, formic, succinic, and lactic acids in fermentation solutions. The acids are extracted by ether, separated by partition chromatography on a column of silica gel using benzene-butanol mixtures, and each determined quantitatively by titration with 0.01 *N* sodium hydroxide using phenol red as indicator. Recoveries are quantitative and determinations accurate within $\pm 2\%$. A method is also given for the quantitative separation and estimation of butyric, propionic, acetic, and formic acids, as well as a modified procedure for preparation of silica suitable for partition chromatography.

Introduction

Bacteria known to ferment glucose to 2,3-butanediol all form organic acids as by-products, sometimes in quite high yields. Those acids most likely to be found are *n*-butyric, acetic, formic, succinic, and lactic. Until recently these were determined in this laboratory by the old established methods based on rate of steam distillation, oxidation reactions, and solubility of the salts (10). These methods have been replaced by a procedure based on the separation of these acids by partition chromatography on silica which is both more rapid and accurate when a variety of acids are to be determined. The purpose of the present paper is to describe this procedure in detail.

The technique of partition chromatography on silica gel was first introduced by Martin and Synge (9) who applied it to separation of the acetamino acids. Tristram (14) has extended their work while Elsdon (2) and Ramsey and Patterson (12) have applied the method to the separation and identification of the volatile saturated fatty acids (C_8 - C_4). Recent work (11, 13) has extended this technique to fatty acid mixtures containing C_5 to C_{10} acids. Isherwood (6) has modified the original method and applied it to the separation and estimation of the organic acids commonly found in fruits. Claborn and Patterson (1) have made use of partition chromatography in determining lactic and succinic acids in foods, but they were unable to separate these acids by chromatography alone. The procedure given below for estimation of the fermentation acids, essentially a modification of Isherwood's method, gives separation of all the fermentation acids mentioned above on one passage through the column.

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Experimental

Reagents

(1) *0.01 N Sodium hydroxide (carbonate-free).*

(2) *0.01 N Hydrochloric acid.*

(3) *0.05% Phenol red solution.*

This was prepared by grinding 0.100 gm. of phenol red in a mortar with 28.5 ml. of 0.01 *N* sodium hydroxide and diluting to 200 ml. with distilled water.

(4) *0.0025% Phenol Red in 0.001 N Sodium Hydroxide.*

This was prepared by mixing 10 ml. of 0.05% phenol red and 20 ml. of 0.01 *N* sodium hydroxide, then diluting to 200 ml. with carbon-dioxide-free distilled water. This solution is used to detect acids in the solvent coming from the column.

(5) *Solvent Mixtures for Developing the Chromatogram*

The best grade of solvents available commercially are used without further purification. All mixtures are made by volume; thus benzene containing 5% of *n*-butanol (BeB₅) is prepared by mixing 5 volumes of *n*-butanol (B) with 95 volumes of benzene (Be). The other mixtures used in the regular procedure are benzene containing 10% *n*-butanol (BeB₁₀) and benzene containing 25% *n*-butanol (BeB₂₅). Before use these mixtures must be equilibrated with the liquid used to wet the silica, in this case 0.01 *N* hydrochloric acid. This is done by shaking 400 ml. of solvent with 80 ml. of 0.01 *N* hydrochloric acid in a one-liter separatory funnel for at least two minutes. After the mixtures have stood for 5–10 min. the aqueous layer is drawn off and discarded and the somewhat turbid benzene phase is filtered through a dry, fast filter paper to remove the remaining droplets of the aqueous phase. The clear, wet solvent is then stored in a 500 ml. Erlenmeyer flask provided with a cork stopper. Mixtures of chloroform and butanol have been quite popular for developing the chromatogram but they are not suitable for separation of succinic and lactic acids.

(6) *Silica Gel Suitable for Partition Chromatography*

The contents of a 1 lb. bottle of reagent grade or "pure" sodium metasilicate (Na₂SiO₃ · 9H₂O) is transferred to a 1 liter graduated beaker, using enough distilled water to give a final volume of 620 ml. The beaker is warmed in a steam bath, with occasional stirring until the silicate is dissolved. Usually the solution is somewhat turbid but filtration is unnecessary. The beaker is then placed in a bath containing ice-water and stirred manually from time to time until the temperature falls to 35° C. During this period enough methyl orange powder is added to give the solution a yellow color. The precipitation is then carried out by adding 10 *N* hydrochloric acid slowly

from a separatory funnel as the solution is being stirred vigorously. The temperature is kept in the range 36° to 38° C. by controlling the rate of addition of the acid. The precipitation passes through a thick stage when the mixture has about the same consistency as porridge but it never actually sets to a gel. It is necessary to beat the mixture thoroughly at this stage. The addition of acid is continued until the indicator remains pink after thorough mixing. It requires about 14 min., approximately 250 ml. being added. A further 10 ml. of acid is then added and the beaker allowed to stand at room temperature for three hours with occasional stirring. More acid is added, in 10 ml. portions, if the indicator loses its pink tinge. The silica is filtered off on a Büchner funnel, washed with three 500 ml. portions of distilled water, resuspended in one-liter of 0.2 *N* hydrochloric acid and allowed to age overnight (18 to 20 hr.). It is then washed on the Büchner funnel until the washings are about pH 4.5 as determined with indicator paper. This requires approximately ten 500 ml. portions of distilled water. Finally it is washed with a 500 ml. portion of 95% ethanol followed by 500 ml. of ethyl ether. After drying in the air on paper for several hours the silica powder is equally distributed between four 250 ml. beakers and dried at 300° to 320° C. for 20 hr. It is stored in a wide-mouth glass-stoppered bottle in a desiccator containing anhydrous magnesium perchlorate. The yield of dry silica is 80 to 82 gm. If equipment for drying the silica at 300° to 320° C. is not available it can be dried satisfactorily at 160° C. in four days.

Apparatus

The apparatus can be assembled from pieces readily available in most laboratories. That needed for separation of the fermentation acids by partition chromatography is shown in Fig. 1. The burette holding the indicator solution is protected from the air by a soda-lime tube and is fitted with a side arm bearing a stopcock (not shown) for refilling. A 500 ml. aspirating bottle, also not shown in the figure, holds a reserve supply of indicator for filling the burette. It is also protected by a soda-lime tube and connected to the side arm of the burette by glass and Tygon tubing. Rubber tubing is avoided since it produces acid on standing in contact with dilute alkali, presumably by oxidation of the sulphur. An enlarged diagram shows how the main stopcock of the burette is grooved by filing to permit easy adjustment of the rate of flow of the indicator solution.

The apparatus used for titration consists of a 2 liter aspirating bottle containing 0.01 *N* sodium hydroxide connected by glass and Tygon tubing to a 10 ml. burette, with a stopcock-bearing side arm. Both the bottle and burette are protected from the air by soda-lime tubes. They are mounted on a large ring stand with a mechanical stirrer arranged so the glass stirrer-blade is 5 to 6 mm. from the bottom of an inverted 250 ml. beaker which is used as a platform for the 150 ml. beaker used in the titration. A bent glass tube with its outlet near the blade of the stirrer serves as an inlet for carbon-dioxide-free air. The tip of the burette should be well inside the 150 ml.

beaker when it is in position. The carbon-dioxide-free air is obtained by passing compressed air from the laboratory lines through a soda-lime tower in series with a gas-washing bottle filled with N sodium hydroxide. This stream

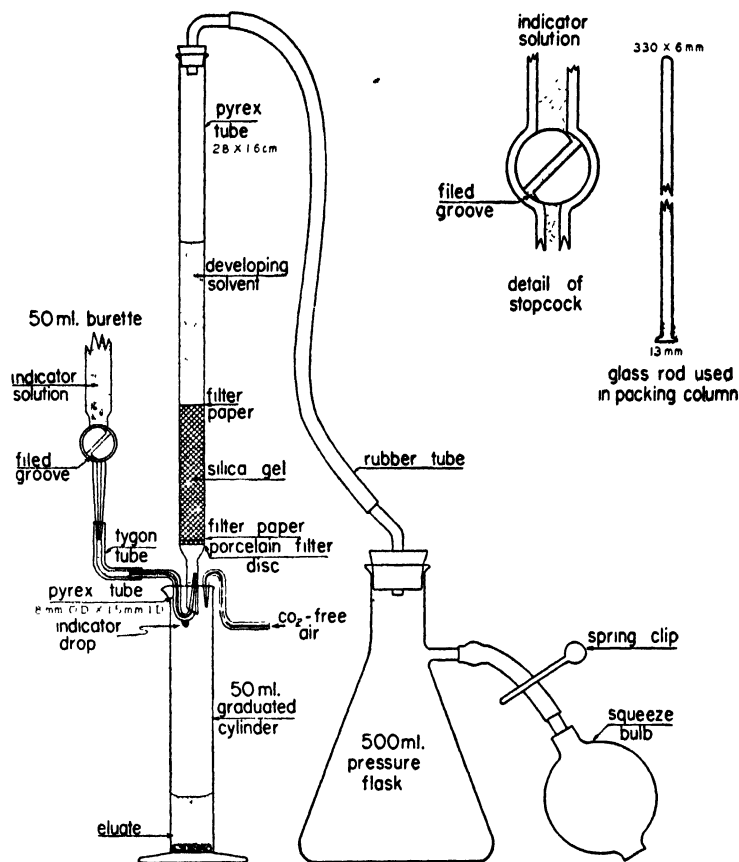


FIG. 1. Apparatus used for chromatographic separation of the fermentation acids.

of purified air is divided into three parts. One part is passed through a bubble counter at the rate of approximately 100 ml. per min. to provide the carbon-dioxide-free air for the apparatus shown in Fig. 1. Another part is used to protect the titrations while the main part escapes through a fritted glass gas dispersion tube immersed in a 1 liter Erlenmeyer flask containing distilled water. This serves as a safety valve and provides a supply of carbon-dioxide-free water for use in the titrations or for preparing the reagents. Water aerated for 10 to 20 min. in this apparatus is practically free of carbon dioxide.

Procedure

(1) Preparation of the Acid Fraction for Partition Chromatography

The fermentation solution is cleared with zinc hydroxide and 100 ml. extracted with ether to remove 2,3-butanediol and other neutral compounds as previously described (10). This is done in order to obtain a fraction for the

determination of 2,3-butanediol rather than to remove any substances that might interfere in the determination of the acids. The aqueous solution left from this extraction is then acidified with an excess of 5 *N* hydrochloric acid (5 to 10 ml.) and extracted for a further 24 hr. as before using a fresh extraction flask containing 50 ml. of anhydrous, reagent grade, ethyl ether but omitting the 20 ml. of water (10). The extract is thoroughly mixed with 25 ml. of *tertiary* amyl alcohol and transferred to a 100 ml. glass stoppered volumetric flask. The mixture is usually monophasic at this stage and ethyl ether is used to rinse out the extraction flask and make the extract to volume. If droplets of water are still apparent a further 10 ml. of *tertiary* amyl alcohol is used. If the fermentation solution is suspected to contain less than 2 milliequivalents of acids per 100 ml. the extraction is performed with only 25 ml. of ether in the extraction flask and the extract made to 50 ml. using 12.5 ml. of *tertiary* amyl alcohol. The extract is stored in a refrigerator until it is convenient to perform the analysis. It is stable for at least two weeks.

In testing the method given in this paper synthetic mixtures of the acids were used. Stock solutions were prepared in the desired solvent (usually ether containing 25% of *tertiary* amyl alcohol) from samples of acids of at least 98% purity. The strength of these solutions was determined by titration and then mixtures were prepared from them volumetrically in order to obtain acid fractions of known composition. The best grade of 85% lactic acid available commercially is not chromatographically homogeneous; it gives a band amounting to approximately 10% of the total acidity which leaves the column before the main lactic acid band. Consequently the lactic acid stock solutions were made by dissolving recrystallized lithium lactate in water, acidifying with hydrochloric acid and extracting with ether as outlined above.

(2) *Preparation of Column for Partition Chromatography*

The chromatogram tube used, shown in Fig. 1, is prepared with the perforated porcelain plate and filter paper disk in position at the bottom. The disks are cut from a fast filter paper with a sharp cork borer. They are slightly larger than the internal diameter of the tube. Three grams of silica, prepared as described above, is weighed to the nearest 0.1 gm. and then mixed with 4.5 ml. of 0.01 *N* hydrochloric acid in a 100 ml. beaker. The silica is stirred with a stainless steel spatula as the acid is added drop by drop. After addition of the acid is complete the mixture is thoroughly blended by mixing and vigorously rubbing it against the sides of the beaker with the spatula for three to four minutes. When this is completed the silica should be a powder with a tendency to adhere to the wall of the beaker. It is slurried with approximately 20 ml. of BeB_5 but quantitative transfer is not necessary. The flocculent suspension in the upper half of the tube is stirred with a glass rod to release any trapped air bubbles. A disk of filter paper is now forced down on top of the gel by the flat-headed glass rod shown in Fig. 1. This rod should have a head only slightly less in diameter than the inside of the chromatogram tube. A firm pressure is maintained until the silica has been

compressed to a length of 8 cm. The supernatant liquid is agitated by raising and lowering the rod and quickly decanted to remove any particles that may have been left in the upper part of the tube. The column is now ready for separation of the acids. If it is inconvenient to start an analysis at once some fresh BeB_5 is poured into the tube; care must be taken at all times to prevent the column from drying out and admitting air. This method of packing gives a firm column that is not easily disturbed by pouring liquids in or out of the chromatogram tube and that shows little change of length during an analysis although pressures up to 50 cm. of mercury are applied. These columns are not subject to cracking.

(3) *Chromatographic Separation and Estimation of the Fermentation Acids*

Before going into detail it is perhaps advisable to give a short description of the procedure and the principles involved. The total acidity of an aliquot of the acid mixture is determined by titration of a small aliquot, and then another aliquot of suitable size is pipetted into a column of silica gel, prepared as described above. As the acid fraction is forced into the column the water held by the silica gel extracts the acids from the organic solvent, those with partition coefficients most in favor of the aqueous phase being extracted most readily. When fresh solvent is forced through the column the acids are extracted back into the solvent phase and pass down the column moving back and forth between the organic and aqueous phases. The acids with partition coefficients most in favor of the organic phase will move most rapidly. As a result the acids separate into bands in the column and the eluate* is made up of fractions containing a single acid separated by fractions free of any appreciable amount of acid. A detailed mathematical description of this separation technique is given by the originators (9). The acids will come out of the column in the order butyric, acetic, formic, succinic, and lactic. The different acid fractions are collected separately and the amount of acid in each is quantitatively determined by titration with sodium hydroxide. In order to know when to change the receiver a slow stream of faintly alkaline phenol red solution is continuously fed into the eluate. The acids are identified by the amount of solvent required to bring them through the column, which is a measure of the partition coefficient. The detailed procedure is as follows.

The total acidity of the acid fraction prepared as described above (usually a mixture of butyric, acetic, formic, succinic, and lactic acids) is determined by titration of a 1 to 2 ml. aliquot to the phenol red end point with 0.01 *N* sodium hydroxide. This titration is performed with 80 to 100 ml. of water containing three drops of the 0.05% phenol red in the 150 ml. beaker of the titration apparatus described above. The tip of the burette should be below the surface and titration finished by adding 0.02 ml. portions of alkali until

* The word "eluate" is used to describe the organic solvent that has passed through the column.

a permanent red-pink color is obtained. In this and all other titrations a stream of carbon-dioxide-free air is continuously bubbled through the mechanically stirred solution.

The supernatant solvent (BeB_5) present in the chromatogram tube is poured out and an accurately measured aliquot of the acid fraction not exceeding 2 ml. (preferably 1 ml. or less) and containing no more acid than can be neutralized by 10 ml. of 0.01 *N* alkali is pipetted onto the silica gel. When doing this the tip of the pipette is held close to the gel and the liquid distributed equally over the surface. Gentle air pressure is applied to the chromatogram tube until the top of the column just barely becomes free of mobile liquid. Care must be exercised at this point to prevent air from getting into the gel. The moment the filter paper on the top of the column breaks through the surface of the liquid the pressure is quickly released by removing the rubber stopper at the top of the chromatogram tube. This is done with the left hand by pushing the stopper sharply to one side with the thumb and index finger while clasping the column with the other fingers. As soon as this operation is complete a 1 ml. portion of the solvent (BeB_5) is added from a pipette, in such a way as to wash down the inside wall of the tube. The receiver is changed to an empty one at this point and the solvent then gently forced into the gel and followed with another 1 ml. portion in the same way. The chromatogram tube is then nearly filled with the developing solvent (BeB_5) and pressure applied until the liquid is flowing through the column at the rate of 3 to 4 ml. per min. (*ca.* three drops per sec.). The indicator solution (0.0025% phenol red in 0.001 *N* sodium hydroxide) is made to flow at approximately one-tenth this rate. The amount of indicator added to each fraction is determined by reading the burette to the nearest 0.1 ml. each time the receiver is changed. Since 50 ml. graduates are used to receive the eluate the amount of developing solvent in each fraction is also known to the nearest milliliter and is recorded. This is necessary for making blank corrections as described below. The indicator drop (see Fig. 1) is watched in order to see when the eluate contains appreciable amounts of acid. If butyric acid is present this drop should turn yellow when a total of approximately 6 ml. of liquid has collected in the receiver. After 5 to 7 ml. more has collected it usually turns pink again; this indicates that the butyric acid is out. A total of 22 ml. is collected and titrated whether the indicator drop has shown acid or not, since as much as 0.30 ml. of 0.01 *N* acid may escape detection. The receiver is changed, the burette read, and development with BeB_5 continued, the chromatogram tube being filled with fresh solvent as required to prevent the column from going dry. After 10 to 20 ml. has been collected the acetic acid is removed in the next 18 to 20 ml. of eluate. A total of 40 to 43 ml. is collected (at least 3 ml. after indicator becomes pink again). The variability in the time of appearance of acetic acid is caused by variation in the amount of acid mixture put on the column. Since the ether - amyl alcohol mixture is a fairly strong developing solvent, analysis of a 2 ml. aliquot results in the acetic acid being carried farther down the column

initially than if a smaller aliquot of the acid fraction is used. When the receiver is changed, after collection of the acetic acid fraction, the supernatant liquid left in the chromatogram tube is *all poured out* and replaced by BeB_{10} . Pressure is again applied and the formic acid fraction (32 ml.) collected. The formic acid starts to come out after 12 ml. and is usually removed by 18 ml. more of eluate. The receiver is changed and the solvent decanted and replaced by BeB_{25} . After approximately 12 ml. has been forced through the column the succinic acid is removed in the next 8 ml. of eluate, a total of 23 ml. being collected. The receiver is changed again and the lactic acid collected in the next 30 ml. It usually starts to come out at 5 ml. and is out by 24 ml. This completes the separation of the acids. The BeB_{25} is poured out and replaced by BeB_5 ; after 15 ml. of this has passed through the column it is ready for the next analysis. Each acid fraction is titrated separately after transferring to the 150 ml. beaker of the titration apparatus using three 20 ml. portions of carbon-dioxide-free water. The 0.01 *N* alkali is run in at a fairly fast rate until the indicator turns pink (in the aqueous phase). The acid in the benzene phase is gradually extracted and the indicator changes back to yellow. More alkali is added intermittently in gradually decreasing amounts, a knowledge of the exact amounts being gained by experience in observing the rate of change of color. The titration is finished by adding 0.02 ml. portions until a pink-red end point is obtained which persists for more than one minute with thorough mixing of the two phases. There is a tendency to under-titrate these fractions until experience is gained with the method. If larger volumes of solvent are to be titrated it is important to make sure enough water is added to give a suspension of the oil-in-water type, rather than *vice versa*, otherwise no end point will be detected, until it is badly overshot.

In practice a fraction is titrated while the next one is being collected, two receivers being used interchangeably. The titrations must be corrected for the alkali in the indicator solution (0.001 *N*) and the "blank" acidity of the solvent. The latter is determined by titrating the developing solvents after they have been equilibrated with the 0.01 *N* hydrochloric acid or preferably after forcing them through a column prepared as used in the analysis. Usually these corrections almost cancel each other but they must be worked out to the nearest 0.01 ml. The alkali is normally present in slight excess and traces of acids in a fraction are determined by back-titration with 0.01 *N* hydrochloric acid. Since the total number of milliequivalents of acid put on the column is known, it is a simple matter to calculate the per cent recovery. If low, this means that some acid more difficult to extract from water than lactic acid was present in the mixture and the development should be continued using BeB_{50} or some other strong solvent mixture. When working with small amounts of acids it should be remembered that a small amount of hydrochloric acid is extracted when acid fractions are prepared by continuous ether extraction. This does not interfere in the determination of the individual acids but makes the "total acids" figure high and may lead one to think some

other organic acid is present. The amount of hydrochloric acid in 1 ml. of the acid fraction is roughly equivalent to 0.03 ml. of 0.01 *N*. This is left on the column during an analysis.

The total time required to develop the partition chromatogram described here is about 45 min. It is customary to analyze three acid fractions completely in about three hours.

The data given above for volumes of developing solvent required to remove the acids from the column are given as a guide but anyone applying this method to unknown solutions should first analyze a synthetic mixture to be more sure of his results. With a constant volume of the acid fraction added to the gel the volumes of solvent required can be reproduced within 1 ml. Actually it would be possible to analyze samples without use of the indicator stream but in fermentation solutions there is always danger of unexpected acids being present.

A column is used for three to four analyses and then discarded. Theoretically it could be used indefinitely but since the acid mixture is not fully saturated with water some of the aqueous phase is removed from the top of the column each time a new sample is analyzed. A column can be preserved under BeB_6 for several days by plugging the exit tube to prevent flow of solvent and then corking the top. Flow of solvent can be prevented by merely stoppering the top but this is not advisable since it allows the bottom of the column to dry out.

(4) *Application of the Method to Mixtures Containing Propionic Acid*

The procedure described above was worked out for a mixture of butyric, acetic, formic, succinic, and lactic acids, which are the only acids encountered so far in 2,3-butanediol fermentations. Since propionic acid is formed in good yield in some other bacterial fermentations a study has been made of the effect of this acid on the determination of those mentioned. When the regular extraction and development procedure is used this acid is found in the butyric acid fraction owing to the strong developing action of the solvents used. If the butyric acid band gives more than 7 ml. of eluate the presence of propionic acid should be suspected. In order to get a reliable estimate of the amounts of each of these acids it is necessary to obtain them in solution in chloroform containing 5% of *n*-butanol (CB_6). Transference of these acids to this solvent should be easily effected by neutralizing a 50 ml. aliquot of the acid fraction with sodium hydroxide, evaporating to dryness on a steam bath, and extracting the residue with CB_6 after mixing it with potassium acid sulphate, as described by Elsdon (2). The other acids will be partially extracted but will not interfere in the analysis. Columns prepared as described above will resolve synthetic mixtures of butyric, propionic, acetic and formic acids, in CB_6 , if operated as follows.

The sample is washed in and development started with chloroform. After 7 ml. of eluate has been collected the butyric acid is obtained in 8 ml.; after a further 8 ml. of nonacidic eluate the propionic is removed by 20 ml. The

solvent is then changed to BeB_8 ; after 25 ml. of neutral eluate the acetic acid is removed in 18 ml. The formic acid is then removed by BeB_{10} in a 16 ml. fraction obtained after 14 ml. of acid-free eluate. The acid fractions are titrated, as usual, to obtain a quantitative estimation of each acid. In practice, formic acid would not be determined in this fraction; the column would be regenerated by BeB_{25} after removal of the acetic acid.

Results and Discussion

The procedure described in this paper differs from previous applications of partition chromatography in some details. Changes have been made in the method of preparing the silica, the technique of packing and operating the column, and in the indicator solution, the developing solvents, the solution used to wet the silica, and the apparatus. Some of the changes made are necessary if resolution of the particular acid mixture obtained in fermentation solutions is to be obtained while other changes, although not absolutely essential, improve its speed or accuracy. The remainder of this paper is devoted to a discussion of results obtained by the method finally adopted and the reasons for modifying the technique of previous workers.

The successful separation of acids by partition chromatography depends primarily on having silica with suitable properties that can be reproduced from batch to batch. The original method of Gordon, Martin and Synge (3) has been modified several times (5, 6, 14) but all workers have used commercial water glass, which varies considerably from one batch to another (4). In an attempt to develop a method that will give reproducible batches of silica the writer has also modified the original procedure (3) by substitution of a purified grade of sodium metasilicate for water glass, by control of the precipitation temperature within specified limits, and by adoption of a higher temperature for drying the silica. The details of the procedure evolved are given in the Experimental Section. Twelve different batches have been prepared from different bottles of sodium metasilicate including the product of two different manufacturers (Merck's and the General Chemical Co.) and all have been found suitable. The need for control of the precipitation temperature is demonstrated by the results in Table I. The water absorbing capacity and apparent fineness of the silica are highest at the lowest precipitation temperatures. This is an effect opposite to that observed by Tristram (14), who found that silica prepared from water glass gave the most porous gels when precipitated at low temperatures. The precipitation temperature adopted in the present work (36° to 38°C.) is a compromise between that giving gels with a reasonably good filtration rate and that giving gels so coarse that the acids are not efficiently separated. It is necessary to cool the solution during the precipitation, otherwise the heat of neutralization will raise the temperature high enough to give gels that are too coarse for a good separation of lactic and succinic acids.

TABLE I

EFFECT OF PRECIPITATION TEMPERATURE ON PROPERTIES OF SILICA GEL

Temperature during precipitation of the silica, ° C.	Ml. of 0.01 <i>N</i> hydrochloric acid used to wet silica (3 gm.)	Length of column, cm.	Rate of flow of solvent, ml./min.	
			Column under pressure of 20 cm. of BeB ₆	Column under 20 cm. of BeB ₆ + 50 cm. of Hg.
28-32	4.0	9.2	0.08	2.0
	5.0	9.2	0.24	4.5
36-38	4.0	8.4	0.16	3.1
	5.0	8.4	0.36	5.6
56-74	4.0	6.1	0.34	7.2
	5.0	*	—	—

* This sample will not absorb 5 ml.; too sticky to use.

The silica obtained has a higher capacity for binding water than that made by previous workers. Good separations of the fermentation acids have been obtained using it wetted with 166% of its weight of water (as 0.01 *N* hydrochloric acid). Other workers used gels wet with only 53% of water (3, 4, 9, 14) while the highest amount used previously is 100% (6). The gels used in the present work are regularly wetted with 150% and give too slow a filtration rate when wetted with smaller amounts. It is necessary to pack the columns by compression with a piston, rather than depending on gravitational forces as previous workers have done. Air pressure must be applied during development to get a convenient rate of filtration. The use of pressure is really convenient since it gives some control over the rate of flow of solvent and permits rates four times as rapid as those used by previous workers to be employed although the columns are intrinsically slower. It is felt that use of the method of packing and developing the chromatogram given above is important since otherwise the most efficient gels prepared would have been discarded as being too slow or for giving weak columns liable to crack.

Most workers have detected the position of the acid bands in the column by incorporating indicators such as methyl orange, bromocresol green, or alphanine-red R (7) into the water used to wet the silica. This is unsatisfactory since the indicators leach more readily than many organic acids, since some indicators are not sensitive enough to indicate the weaker acids (i.e., butyric), and since it is desirable to wet the silica with a dilute mineral acid in order to prevent tailing of the bands (6, 8). Isherwood introduced the use of thymol blue used externally to overcome these objections (6). He wet the silica with 0.5 *N* sulphuric acid to suppress tailing. In the present work it was found necessary to change this to 0.01 *N* hydrochloric acid to prevent decomposition of the formic acid (see Table II). Phenol red has been substituted for thymol blue because it gives a more accurate end point for the titration. The apparatus has been modified to permit accurate measurement

TABLE II
STABILITY OF FORMIC ACID IN SILICA GELS

Solution used to wet silica*	Method of preparation of silica**	Time in gel, hr.	As ml. of 0.01 N		% Recovered
			Formic acid added	Formic acid recovered	
0.5 N H ₂ SO ₄	Isherwood's	1.7	4.41	3.82	86.6
"	"	3.7	4.41	2.68	60.6
"	"	17.0	4.41	0.88	19.9
"	Modified procedure	3.0	10.98	8.80	80.1
"	"	19.0	10.98	3.74	34.0
0.01 N HCl	"	3.0	10.98	11.00	100.2
"	"	19.0	10.98	10.11	92.2
Water	Isherwood's	2.4	4.41	4.50	102.1

* In wetting silica prepared by Isherwood's method (6), 3 ml. of solution was used, while 4 ml. was used for silica prepared by the modified procedure.

** The "modified procedure" is that given in detail in this paper.

of the indicator added to each fraction, to minimize holdup in the detection system and to protect the alkaline indicator solution from the carbon dioxide of the ambient atmosphere.

Mixtures of the fermentation acids of known composition can be analyzed with $\pm 2\%$ error, as shown in Table III. The chief difficulty lies in titration of the small amounts of acid involved. Particular attention has been paid

TABLE III
DETERMINATION OF FERMENTATION ACIDS IN SYNTHETIC MIXTURES
BY PARTITION CHROMATOGRAPHY*

Expt. No.	As ml. of 0.01 N											
	Added						Recovered					
	Butyric	Acetic	Formic	Succinic	Lactic	Malic	Butyric	Acetic	Formic	Succinic	Lactic	Malic
1	—	—	—	3.34	3.46	—	—	—	—	3.28	3.50	—
2	—	—	—	1.33	10.39	—	—	—	—	1.32	10.37	—
3	—	—	—	10.02	1.73	—	—	—	—	10.01	1.73	—
4	—	—	—	16.70	8.65	—	—	—	—	16.72	8.61	—
5	3.74	4.41	4.38	2.67	3.46	—	3.69	4.40	4.30	2.65	3.48	—
6	1.49	4.42	1.74	1.29	0.69	—	1.51	4.44	1.72	1.29	0.69	—
7	0.75	0.89	8.76	1.29	1.38	—	0.76	0.93	8.74	1.29	1.36	—
8	1.49	1.76	1.75	2.58	6.92	—	1.51	1.73	1.74	9.50	—	—
9	0.74	0.88	0.87	1.29	3.46	—	0.74	0.89	0.87	1.28	3.44	—
10	1.86	2.25	2.34	1.78	1.81	—	1.87	2.25	2.34	1.77	1.80	—
11	1.55	1.87	1.95	1.45	1.54	2.50	1.53	1.82	1.94	1.47	1.53	2.46

* Acids were dissolved in ethyl ether containing 25% of tertiary amyl alcohol.

to the determination of lactic and succinic acids, which, of all pairs of fermentation acids studied, are the most difficult to separate. Attempts to separate them using chloroform-butanol mixtures have failed (1) but they can be

separated fairly well if mixtures of butanol with aromatic hydrocarbons (benzene, toluene, xylene) or methyl isobutyl ketone are used. In the first four experiments (Table III) they were put on the column in 1 ml. of solvent and the column was developed with BeB_{25} only. Under these conditions a sample containing twice as much acid as recommended in the procedure could be analyzed successfully. However when the full development procedure is used a good separation between these acids is not obtained if the column is overloaded (Expt. 8, Table III). In Expt. 9, the same mixture used as in Expt. 8 was analyzed successfully by using one-half the quantity. That is why it is recommended that the sample taken for analysis contain not more than 0.1 milliequivalents of acid.

As mentioned above, the purpose of adding a strong acid to the aqueous phase is to suppress ionization of the fermentation acids and thus prevent tailing. If this condition is realized the concentration of acids in the eluate should give a curve resembling the normal curve of error when plotted against volume of eluate (9). Such a concentration curve is shown in Fig. 2, for the

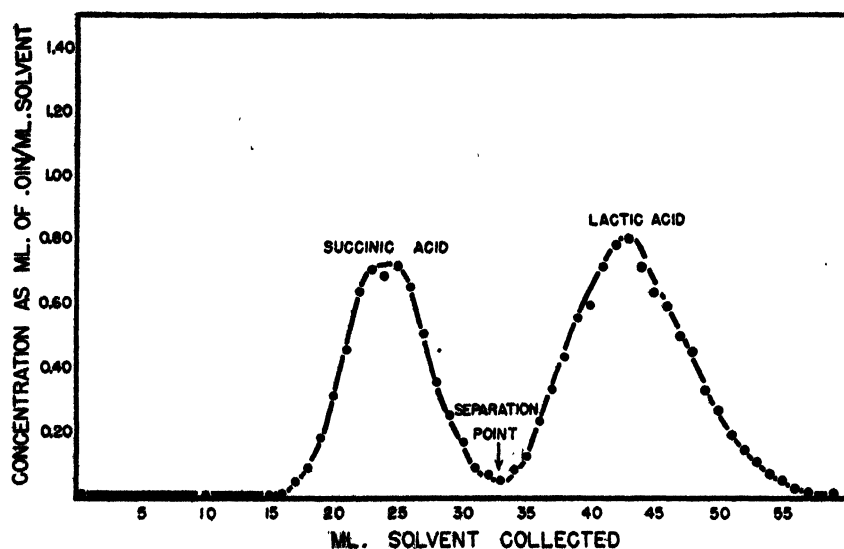


FIG. 2. Concentration curves for chromatographic separation of succinic and lactic acids.

separation of succinic and lactic acids. It is apparent that there is little sign of tailing even with these comparatively strong acids, and consequently that the gel is acting according to the theory of liquid-liquid extraction (9). In obtaining the data for this figure the column was overloaded 46% above the recommended amount in order to have more accurate titrations for the numerous small fractions. The amount of succinic acid added was equivalent to 5.93 ml. of 0.01 *N* (recovered 5.92) while the lactic acid added was equivalent to 8.66 ml. (recovered 8.65). It is apparent from Fig. 2 that the separation is not quite complete in spite of the good results obtained. The method of indication used in this paper is deliberately made insensitive

enough to detect separations like this, and thus give answers accurate within $\pm 2\%$, where a highly sensitive method of detection would show only one acid band.

The procedure given in the experimental section for analysis of mixtures containing propionic acid is based on the results shown in Table IV. When the regular extraction and development procedure was used propionic acid

TABLE IV
DETERMINATION OF VOLATILE ACIDS IN SYNTHETIC MIXTURES

Experiment No.	Solvent used in preparing mixture	Development procedure*	As ml. of 0.01 N							
			Added				Recovered			
			Butyric	Propionic	Acetic	Formic	Butyric	Propionic	Acetic	Formic
1	Ethyl ether plus 25% tertiary amyl alcohol	Regular procedure	2.07	0.68	2.48	2.92	2.76	Nil	2.48	2.91
2			2.07	2.05	2.48	2.92	4.07	Nil	2.52	2.90
3			2.07	3.45	2.48	2.92	5.48	Nil	2.50	2.96
4	Ethyl ether plus 25% tertiary amyl alcohol	Carbon tetrachloride followed by regular procedure	2.07	0.68	2.48	2.92	2.10	0.65	2.47	2.90
5			2.07	2.05	2.48	2.92	2.70	1.47	2.51	2.88
6			2.07	3.45	2.48	2.92	3.27	2.23	2.54	2.90
7	Chloroform plus 5% n-butanol	Carbon tetrachloride followed by regular procedure	2.04	0.74	2.33	2.55	0.71	2.08	2.31	2.55
8			3.40	2.24	—	—	1.95	3.71	—	—
9			3.23	2.04	—	—	2.01	3.26	—	—
10			5.42	—	—	—	3.62	1.80	—	—
11	Chloroform plus 5% n-butanol	Chloroform followed by regular procedure	5.42	—	—	—	5.41	—	—	—
12			3.23	2.04	—	—	3.24	1.98	—	—
13			2.04	0.74	2.40	2.55	2.06	0.73	2.39	2.51
14			2.04	3.67	2.40	2.55	2.03	3.65	2.41	2.52
15			3.40	3.67	2.40	2.55	3.41	3.61	2.41	2.48

* The "regular procedure" is that given in detail in the Experimental Section of this paper for mixtures not containing propionic acid; 1 ml. of acid fraction put on the column.

was not separated from butyric acid (Expts. 1 to 3) but it had the effect of doubling the volume of acidic eluate collected as the butyric acid fraction. If the column is first developed with carbon tetrachloride, separate bands of butyric and propionic acid are formed (Expts. 4 to 6). The butyric band comes between 5 and 10 ml. of eluate; after changing to BeBr_2 the propionic band is collected in 13 ml. after 9 ml. of neutral eluate. However, the figures for butyric acid are high while those for propionic acid are low by an equal amount. It appears that the acid band due to propionic has been distorted so that it gives two maxima. This can be explained as due to the strong developing action of the mixture of ether and amyl alcohol in which the acids were dissolved in these experiments. It carries them both far down the column but the propionic acid is partially extracted into the aqueous phase.

On developing with carbon tetrachloride part of the propionic acid is removed with the butyric while the most of the rest comes off quite a bit later. It should be possible to avoid this phenomenon by having the acids dissolved in a mixture with less developing action. Consequently the acids were dissolved in chloroform containing 5% of butanol, and the developing procedure, starting with carbon tetrachloride, was again applied (Expts. 7 to 10). The same type of behavior was found except this time it was the butyric acid that formed two bands. This is best shown in Expt. 10 in which butyric acid was the only one put on the column yet two distinct bands were formed. After 8 ml. of carbon tetrachloride was collected the indicator showed acid for 18 ml.; the solvent was changed to BeB_3 and after 10 ml. with "no acid" the eluate was acidic for 6 ml. more. It is inconvenient to use a weaker solvent for the acid mixture; however, one can expect to prevent this "band-splitting" by using a stronger developing solvent in this case. Therefore carbon tetrachloride was replaced by chloroform and in this way satisfactory analyses of mixtures of the volatile fatty acids obtained (Expts. 11 to 15).

All the results given above were obtained using synthetic mixtures of acids. However the procedure has been successfully applied to glucose solutions fermented by *Aerobacter aerogenes*, *Bacillus polymyxa*, *Bacillus subtilis* (Ford's type) and *Serratia marcescens* (work, as yet, unpublished).

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UNE NOUVELLE SYNTHÈSE DE L'ACIDE AMINOADIPIQUE¹

PAR ROGER GAUDRY

Résumé

L'acide α -aminoadipique a été préparé avec un rendement de 48% à partir de l'acide α -amino- ϵ -hydroxycaproïque par oxydation de son dérivé benzoylé en acide α -benzoylaminoadipique, suivie d'hydrolyse du groupement benzoyle. Le dérivé phtalylé fut aussi préparé à partir de l'acide α -aminoadipique et de l'anhydride phtalique, de même que par oxydation de l'acide α -phtalimido- ϵ -hydroxycaproïque, mais cette dernière méthode ne donne que de faibles rendements.

Introduction

Récemment, Borsook et ses collaborateurs (2) ont démontré que l'acide α -aminoadipique est un produit de métabolisme de la lysine, et est même susceptible de remplacer celle-ci dans les milieux de culture de certains micro-organismes.

Mais l'acide α -aminoadipique n'est pas une substance facilement accessible. Il a d'abord été synthétisé par Sørensen (6), par condensation du phtalimido-malonate d'éthyle et du γ -chlorobutyronitrile, suivie d'hydrolyse, ensuite par Dieckmann (3), par réduction de l'acide α -oximinoadipique.

Nous avons pensé qu'il serait possible d'en élaborer une synthèse plus pratique à partir de l'acide α -amino- ϵ -hydroxycaproïque, dont nous avons récemment publié la synthèse (4), et qu'on peut maintenant préparer en grandes quantités à partir du dihydropyrane.

La méthode que nous avons utilisée est celle mise à point par Klostermann et Painter (5) pour la synthèse de l'acide aspartique à partir de l'acide α -amino- γ -hydroxybutyrique. Nous avons benzoylé l'acide α -amino- ϵ -hydroxycaproïque (I) avec le chlorure de benzoyle, et nous avons oxydé l'acide α -benzoylamino- ϵ -hydroxycaproïque (II) en acide α -benzoylaminoadipique (III) au moyen du permanganate de potassium en milieu alcalin. L'hydrolyse du groupement benzoyle par l'acide chlorhydrique dilué a donné l'acide α -aminoadipique (IV) avec un rendement de 48% à partir de l'acide α -amino- ϵ -hydroxycaproïque (I).

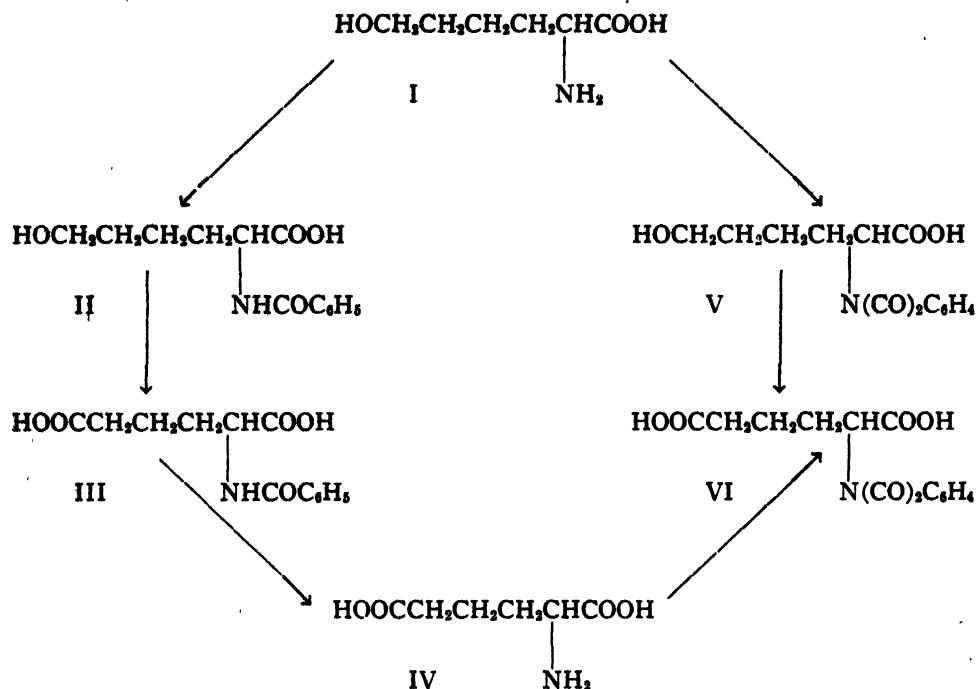
Une autre possibilité consistait à utiliser le dérivé phtalylé (V) de l'acide α -amino- ϵ -hydroxycaproïque, au lieu du dérivé benzoylé. Nous l'avons préparé en chauffant un mélange d'anhydride phtalique et d'acide aminé, d'après la méthode de Billman et Harting (1), et nous l'avons oxydé en acide α -phtalimidoadipique (VI), identique au produit obtenu en chauffant l'acide α -aminoadipique avec l'anhydride phtalique. Mais parce que l'acide α -phtalimido- ϵ -hydroxycaproïque ne s'obtient qu'avec un rendement de 8%, à com-

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Contribution du Département de Biochimie de la Faculté de Médecine, Université Laval, Québec, Qué.

parer avec 80% pour le dérivé benzoylé, cette modification de la méthode ne présente qu'un intérêt théorique.

Comme c'est par hydrolyse de la 5- δ -hydroxybutylhydantoïne que nous obtenons l'acide α -amino- ϵ -hydroxycaproïque (4), il eut été avantageux d'oxyder directement cette hydantoïne en l'hydantoïne correspondant à l'acide α -aminoadipique, sans passer par le dérivé benzoylé. Malheureusement, nos essais furent infructueux.



Partie expérimentale

Acide α -benzoylamino- ϵ -hydroxycaproïque (II)

Dans un ballon à trois cols de 500 ml. plongé dans un bain de glace et d'eau, muni d'un thermomètre, d'un agitateur et de deux entonnoirs à décanter, on place 14.7 g. (0.1 mole) d'acide α -amino- ϵ -hydroxycaproïque, 100 ml. d'une solution normale de soude caustique et quelques gouttes d'une solution de phénolphthaléine. En maintenant le mélange entre 0 et 10° C., on ajoute goutte à goutte, simultanément, 12 ml. de chlorure de benzoyle et 100 ml. de soude normale, en réglant les vitesses d'addition de telle sorte que le mélange réactionnel soit constamment alcalin. On continue d'agiter pendant une heure, on acidifie avec 30 ml. d'acide chlorhydrique concentré, on porte à la glacière jusqu'à ce que le précipité blanc soit cristallin, on le filtre à succion, on le lave dans un mortier avec de l'éther, on le filtre à nouveau, et on le sèche à l'air. Rendement brut, 24.5 g., 97.7%. Pour le recrystalliser, on le dissout dans un petit volume d'alcool éthylique bouillant (environ 25 ml.), on refroidit et on ajoute un grand volume d'éther (250 ml.). Quand la cristallisation est terminée, on filtre à succion le précipité, on le lave à l'éther sur le filtre et on

le sèche. Rendement: 21 g., 80%. P.f. 144° à 146°.* Calculé pour $C_{13}H_{17}O_4N$: N, 5.57%. Trouvé: N, 5.60%.

Acide α -benzoylaminoadipique (III)

A une solution de 25.1 g. d'acide α -benzoylamino- ϵ -hydroxycaproïque (0.1 mole) dans 200 ml. d'une solution normale de soude caustique, on ajoute lentement 21 g. de permanganate de potassium, en agitant constamment, et en ayant soin de tenir le mélange réactionnel dans un bain d'eau froide (environ 10° C.). Quand la coloration due au permanganate est entièrement disparue (ce qui nécessite trois à quatre heures), on filtre à succion le bioxyde de manganèse, on acidifie la solution incolore avec 50 ml. d'acide chlorhydrique concentré, on mélange et on porte aussitôt à la glacière. Lorsque la cristallisation est terminée, on filtre à succion, et on recrystallise aussitôt en dissolvant le précipité dans 250 ml. d'eau bouillante. Après refroidissement, on filtre et on sèche à l'air. Rendement: 20 g., 75%. P.f. 184° à 185°. Litt. (6): 184°. Calculé pour $C_{13}H_{15}O_5N$: N, 5.28%. Trouvé: N, 5.32%.

Acide α -aminoadipique (IV)

A une solution de 26.5 g. d'acide α -benzoylaminoadipique (0.1 mole) dans 300 ml. d'eau bouillante, on ajoute 200 ml. d'acide chlorhydrique concentré, et on fait bouillir à reflux pendant six heures. Après refroidissement, on filtre à succion l'acide benzoïque, et on évapore le filtrat dans le vide. On dissout le résidu huileux dans 200 ml. d'alcool éthylique absolu bouillant, on ajoute 12 ml. de pyridine, et on porte à la glacière. On filtre à succion le précipité blanc, et on le lave au mortier avec de l'alcool absolu pour éliminer les dernières traces de pyridine, et on le sèche à l'air. Rendement: 12.9 g., 80%. P.f. 185° à 189° avec dégagement de gaz. Calculé pour $C_8H_{11}O_4N$: N, 8.69%. Trouvé: N, 8.47%.

Acide α -phthalimidoadipique (VI) à partir de l'acide α -aminoadipique

On mélange intimement dans un mortier 1.6 g. d'acide α -aminoadipique et 1.4 g. d'anhydride phthalique et on chauffe à 180° C. pendant 10 min. dans un bain d'huile. Par refroidissement on obtient un solide blanc qu'on recrystallise de l'eau bouillante. Rendement: 2.1 g., 70%. P.f. 227° à 229°. Calculé pour $C_{14}H_{13}O_6N$: N, 4.81. Trouvé: N, 4.79%.

Acide α -phthalimido- ϵ -hydroxycaproïque (V)

On chauffe à 180° C. dans un bain d'huile, pendant 10 min., un mélange intime de 10 g. d'acide α -amino- ϵ -hydroxycaproïque et de 10 g. d'anhydride phthalique. On dissout la masse refroidie de l'alcool dilué chaud. Par refroidissement, il se sépare une abondante couche huileuse. On décante alors la solution surnageante, qu'on laisse s'évaporer dans une capsule de porcelaine. On obtient alors un fin précipité blanc, cristallin. Rendement: 1.3 g., 8%. P.f. 162° à 163°. Calculé pour $C_{14}H_{15}O_6N$: N, 5.05%. Trouvé: N, 5.04%.

*Les points de fusion ne sont pas corrigés.

Acide α -phtalimidoadipique (VI) à partir de l'acide α -phtalimido- ϵ -hydroxycaproïque

A une solution de 3 g. d'acide α -phtalimido- ϵ -hydroxycaproïque dans 50 ml. d'une solution demi-normale d'hydroxyde de sodium, on ajoute lentement 2.2 g. de permanganate de potassium, en maintenant le mélange à la température de la chambre. Après quatre heures d'agitation, on ajoute quelques gouttes d'alcool méthylique pour réduire l'excès de permanganate, on filtre le bioxyde de manganèse, on acidifie le filtrat limpide et incolore avec 5 ml. d'acide chlorhydrique concentré et on porte à la glacière. On filtre à succion le précipité et on le recrystallise dans 25 ml. d'eau bouillante. Rendement: 0.5 g., 15%. P.f. 224° à 226°. Un point de fusion mélangé avec l'acide α -phtalimidoadipique obtenu à partir de l'acide α -aminoadipique a donné 226° à 227°.

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THE TESTING OF ACTIVATED CHARCOALS BY THE ISOPIESTIC METHOD¹

BY H. SHEFFER,² K. T. WALDOCK³ AND J. B. FERGUSON⁴

Abstract

The isopiestic method has been applied to the testing of activated charcoals. The ratios of vapor adsorbed at saturation were found to agree well with the ratios of the activities obtained by a flow method. The sorptive capacities of nine different activated charcoals for carbon tetrachloride, water, amyl chloride, benzene, methyl alcohol, *n*-hexane, mustard gas, and phosgene have been compared. A simple, rapid method for testing charcoals is suggested.

One of the standard methods for measuring the "activities" or sorptive powers of activated charcoals involves the use of a flow system (7, 3). Air containing a definite concentration of carbon tetrachloride is passed through a specified volume of charcoal until a detectable trace of vapor appears in the effluent air. From the weight of carbon tetrachloride adsorbed the "volume activity" ($V.A.$ = grams of carbon tetrachloride adsorbed per 100 cc. of charcoal) is obtained. This empirical method has been criticized by Allmand and Manning (1) and by Chaney, Ray, and St. John (2), not only because of its tediousness, but because factors that bear no relation to the intrinsic character of the charcoal may affect the results considerably.

In 1941 Dr. R. A. Robinson suggested that an attempt be made to apply the isopiestic equipment of these laboratories to the study of activated charcoals. Sinclair (10) and Robinson and Sinclair (8) made the greatest improvements in the isopiestic or isotonic method in their application of it to the measurement of vapor pressures of aqueous solutions. The historical and theoretical development of this method has been summarized by Janis and Ferguson (5). The underlying principle is the equilibration of solutions to the same vapor pressure by distillation of vapor from one solution to another under vacuum. It was thought that vapor distribution, in this manner, among charcoals would yield information as to their relative sorptive capacities.

The present investigation deals with such equilibrium measurements and their significance. A simple method is suggested for testing activated charcoals rapidly and easily, the results having at least as much value as the standard $V.A.$ measurement.

Experimental and Results

The Isopiestic Method

Since the accuracy of the vapor pressure measurements for aqueous solutions was not required for the charcoals, the copper block and silver dishes used by

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Sheffer, Janis, and Ferguson (9) were not employed in these experiments. The charcoal samples were weighed into weighing bottles which were placed in a desiccator along with the required amount of carbon tetrachloride. The desiccator was carefully evacuated and allowed to stand until equilibrium was attained, after which dry air was allowed into the desiccator and the gain in weight of the charcoal samples obtained. It was found that a grease made by partially saponifying linseed oil was satisfactory for the retention of carbon tetrachloride vapor. When it was desired to place the desiccator in water in a thermostat, this greasy "soap" was used on the inner half of the flange of the desiccator while ordinary stopcock grease was used on the outer half. In most of the experiments it was found that thermostatically controlling the desiccator was unnecessary. Particularly near saturation, slight variations in temperature affected all samples proportionately.

All charcoal samples used were air-dried at 110° C. to constant weight. The sample numbers and corresponding *V.A.*'s as determined by the supplier are given in Table I. The charcoals were all from coconut shell, activated in

TABLE I
COMPARISON OF ISOPIESTIC AND FLOW METHOD ACTIVITIES

Charcoal No.	Isopiestic ratio near saturation $\frac{(W.A.)_s}{(W.A.)_i}$	Average bulk density	Calculated <i>V.A.</i> (isopiestic)	Supplier's <i>V.A.</i> (flow method)
1	0.670	0.556	14.8	13.2
2	0.655	0.519	13.5	13.7
3	0.760	0.547	16.6	17.8
4	0.827	0.560	18.4	18.0
5	1.055	0.444	18.7	20.3
6	1.095	0.495	21.6	21.3
7	1.000	0.535	St'd.	21.3
8	1.085	0.502	21.7	21.5
9	1.100	0.529	23.2	23.6

different ways and sprayed with various catalysts. The carbon tetrachloride used was a C.P. grade dried over sodium hydroxide.

In a preliminary experiment one sample of charcoal was allowed to adsorb approximately 30% by weight of carbon tetrachloride vapor. This sample, together with an uncharged one of the same charcoal, were placed in a desiccator under vacuum. It was found that the carbon tetrachloride distilled from the charged to the uncharged sample until both were within 1% of the same concentration.

To obtain the rate of attainment of equilibrium, two samples of each of two different charcoals were placed in a desiccator, together with a dish containing the desired amount of carbon tetrachloride. The desiccator was then partially evacuated and allowed to stand until all the carbon tetrachloride was adsorbed by the charcoals (about 15 min.). The residual air was then removed by

further evacuation and the desiccator was placed in a thermostat until equilibrium was reached. The samples were periodically removed and weighed and when the concentration of like pairs agreed closely it was considered that equilibrium had been attained. In this way it was found that equilibrium was reached very slowly at low concentrations, e.g., at concentrations around 10% of the saturation value the samples were not at equilibrium even after four days. At concentrations in the neighborhood of 25% of saturation, two days were sufficient for attainment of equilibrium, this time decreasing to 24 hr. at 50% and to only two to three hours at saturation.

Charcoal No. 7 was arbitrarily chosen as a standard in the intercomparison of the various charcoal samples by the above method. The isopiestic ratio for two charcoals is defined as the ratio of the weights of adsorbed material per gram of charcoal at equilibrium, the weight for the standard being the divisor. In the isopiestic curves shown in Fig. 1 the isopiestic ratios are

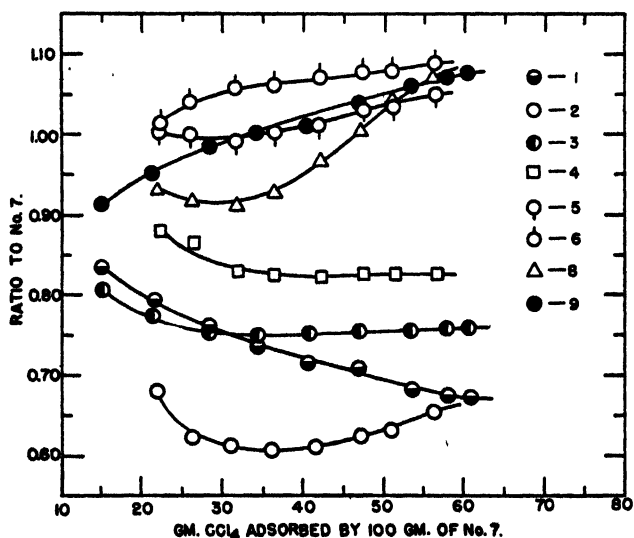


FIG. 1. *Isopiestic ratio curves with charcoal No. 7 as standard.*

plotted against the corresponding weight percentage (grams per 100 gm. of charcoal) for the standard, No. 7. It is evident from these curves that the charcoals vary considerably in their relative pickup over the range of partial pressures involved. The ratios corresponding to the lower partial pressures are of interest in considering the use of charcoals at low pressures. All the curves tend to flatten out near saturation and it is only in this region that ratios are obtained that are at all comparable with those obtained from the *V.A.*'s of the flow method.

In order to make this comparison it was necessary to obtain the bulk densities of the charcoals, since the isopiestic determinations were on a weight basis. The bulk density of each was determined by placing approximately 20 cc. of the charcoal in a 25 cc. graduate, tapping to maximum density, and

weighing the known volume. By this method the values were reproduced to better than 1%. The average values of the bulk densities (*B.D.*) are given in Table I.

The *V.A.*'s were calculated from the isopiestic results using No. 7 as a standard. If we define the weight activity, *W.A.* = grams carbon tetrachloride adsorbed per 100 gm. charcoal, near saturation, then the *V.A.*'s may be calculated using the following equation:

$$(V.A.)_s = \frac{(W.A.)_s}{(W.A.)_7} \cdot \frac{(B.D.)_s}{(B.D.)_7} \cdot (V.A.)_7.$$

The values calculated in this manner are compared with those from the flow method in Table I. The discrepancy between the two methods amounts to about 11% for charcoal No. 1, but is much less for all the others.

The Flow Method

In order to determine the significance of the isopiestic results in relation to the *V.A.* values given by the charcoal supplier, a flow apparatus was set up. This apparatus was a simplified version of the type described by Mantell (7). The charcoal container was a glass tube 1 cm. in diameter. It was found that when the charcoal column was 15 cm. long, results were obtained that were comparable with those of the supplier's. The over-all rate of air - carbon tetrachloride flow was approximately 1000 cc. per min. in each measurement, the concentration of carbon tetrachloride being allowed to vary within limits as indicated in Column 2 of Table II. As before, the actual determinations were made on a weight basis and from these the *V.A.*'s were calculated. The results, given in Table II, indicate considerable variation in the *V.A.* values (Column 4) for each charcoal. Both the supplier's and the isopiestic *V.A.* values lie within this range of deviation.

It may be noted that no simple relation exists between the rate of adsorption and these variations. This point was further investigated using a sample of charcoal No. 3 at a rate of 0.0798 gm. per min. (approximately double the rate of adsorption), keeping the over-all rate of air the same as before. This gave a *V.A.* of 18.7 for No. 3, indicating that the radical change in rate did not materially alter the *V.A.* value.

It was found, however, that for a constant concentration of carbon tetrachloride, in the air stream, the *V.A.* increased as the air rate decreased, as might be expected. When the rate of adsorption was normal, halving the total flow was found to increase the *V.A.* of No. 3 to 20.9 and of No. 7 to 25.6. Although these values differ considerably from those obtained at the normal flow rate, their *ratio* is approximately the same as the ratio of the normal *V.A.*'s. The ratios, therefore, are less affected by the experimental conditions than the actual *V.A.*'s and it is the former that are given by the isopiestic comparison.

TABLE II
VARIATIONS IN ACTIVITIES FROM FLOW METHOD

Charcoal No.	Gm. CCl_4 adsorbed/min.	Weight activity	Volume activity	Average V.A.	Supplier's V.A.
1	0.0390	21.3	11.5	12.5	13.2
	0.0410	22.3	12.4		
	0.0420	25.1	13.9		
	0.0450	21.7	12.1		
3	0.0364	31.3	17.1	18.0	17.8
	0.0370	33.8	18.5		
	0.0371	36.4	19.9		
	0.0410	32.0	17.5		
	0.0458	30.8	16.9		
4	0.0398	32.0	17.9	18.4	18.0
	0.0450	33.8	19.0		
5	0.0335	46.5	20.7	20.9	20.3
	0.0340	47.5	21.1		
7	0.0355	43.8	23.4	22.0	21.3
	0.0368	39.5	21.1		
	0.0375	40.4	21.6		
8	0.0336	46.7	23.4	22.9	21.5
	0.0375	48.5	24.3		
	0.0375	43.7	21.9		
	0.0423	44.0	22.0		
9	0.0338	44.2	23.4	24.3	23.6
	0.0350	47.1	24.9		
	0.0362	46.1	24.4		
	0.0364	47.9	25.4		
	0.0376	45.0	23.8		
	0.0443	45.7	24.2		

In order to gain further information as to the significance of the V.A. values as obtained by the flow method, it was decided to obtain the concentration gradient of adsorbed carbon tetrachloride through the charcoal bed. For this determination the charcoal column was divided into four approximately equal sections by means of glass wool plugs, each section of charcoal being accurately weighed before and after testing. Although the true concentration gradient could not be obtained from so few measurements, the approximate shape of the curve was indicated. Typical results are shown in Fig. 2.

The general shapes of the curves are quite similar and it can be seen that the volume activities, which are, of course, proportional to the areas under each curve, are governed mainly by the top parts of the curves, i.e., where the charcoals are *nearly saturated*. This shows why the isopiestic ratios near saturation give comparable results. A comparison of the two curves for No. 3 in Fig. 2 shows that the charcoal in the first part of the tube is more nearly saturated at the higher adsorption rate, but that the gradients for the lower part of the tube are such that the areas and the V.A.'s are practically identical.

It has been pointed out from the results in Table I that the isopiestic *V.A.* for charcoal No. 1 was considerably higher than that from the flow method. In Fig. 2 it is seen from the gradient curve for No. 1, that there is a considerable

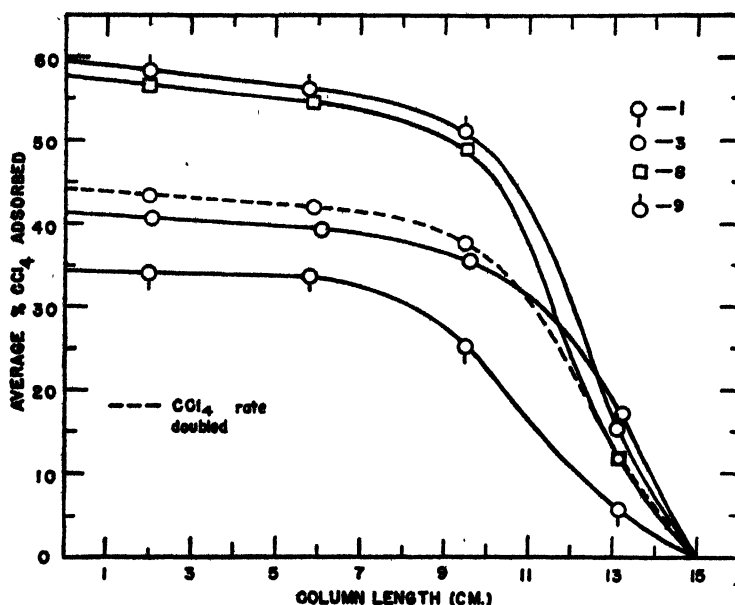


FIG. 2. Concentration gradients of adsorbed carbon tetrachloride in charcoal columns after flow testing.

area under the sloping part of the curve so that, in this case, the *V.A.* is not governed as much by the saturation value. If a longer charcoal column had been used, the relative increase in area under the upper part of the curve would have given results more comparable with the isopiestic values.

Procedure for Obtaining Isopiestic Ratios Near Saturation

Since the saturation values control the *V.A.*'s, it was desirable to determine the simplest procedure for obtaining these isopiastically. In Table III the

TABLE III
ISOPIESTIC ACTIVITIES NEAR SATURATION

Charcoal No.	Run 1		Run 2		Run 3		Run 4		Supplier's <i>V.A.</i>
	<i>W.A.</i>	<i>V.A.</i>	<i>W.A.</i>	<i>V.A.</i>	<i>W.A.</i>	<i>V.A.</i>	<i>W.A.</i>	<i>V.A.</i>	
1	46.5	14.2	39.9	14.4	45.5	15.3	47.1	15.6	13.2
2	48.0	14.0	38.2	13.7	44.6	13.9	46.9	14.5	13.7
3	54.3	16.7	47.5	17.0	53.4	17.9	55.2	18.1	17.8
4	56.8	17.8	49.8	18.2	51.3	17.7	53.0	17.8	18.0
5	76.0	18.9	65.9	19.1	71.2	19.6	74.9	20.0	20.3
6	76.8	St'd.	66.0	St'd.	74.0	22.4	77.2	22.9	21.3
7	73.5	22.0	62.3	21.7	70.2	23.0	71.5	22.8	21.3
8	75.0	21.1	64.6	21.2	68.0	21.0	70.4	21.2	21.5
9	72.5	21.6	63.0	21.8	72.5	St'd.	74.4	St'd.	23.6

weight activities obtained by various procedures are given. The *V.A.*'s, calculated from these by taking one charcoal as standard and using the bulk densities given in Table II, are also shown.

In *Run 1* approximately 3 gm. of each sample was used, two hours being allowed for the attainment of equilibrium at saturation. These samples were returned (without additional carbon tetrachloride) to the desiccator after weighing, and, after evacuation, allowed to stand a second two hours, after which the results given for *Run 2* were obtained. No. 6 was taken as standard.

In *Run 3*, 6 to 7 gm. of each charcoal was used and three hours were allowed for saturation, after which dried air was allowed into the desiccator and five minutes allowed for any condensed carbon tetrachloride to evaporate from the open weighing bottles. In *Run 4* these same samples remained in the evacuated desiccator overnight along with excess carbon tetrachloride. The results so obtained did not differ radically from those of *Run 3* so that equilibrium must be closely approached in three hours.

To show that the discrepancies in the results are due to nonuniformity of the samples and not to lack of equilibrium, six samples of No. 5 were compared in the same manner as in *Run 3*. The weight activities at saturation after three hours were as follows: 74.8; 73.3; 72.7; 71.8; 71.7; 77.6. The excess carbon tetrachloride being removed, the samples were returned to the desiccator which was completely evacuated and allowed to stand in a thermostat for 48 hr. The following values were then obtained: 66.7; 65.1; 64.4; 64.2; 63.9; 68.8. The discrepancies were still of the same magnitude, indicating the nonuniformity of the average surface of the charcoal and the fact that equilibrium is rapidly approached.

Final Test Procedure

The procedure for *Run 3* was adopted as most suitable because of its simplicity and reliability. A vacuum desiccator of 6½ in. internal diameter was used. In this vessel nine weighing bottles (40 by 50 mm.) fitted snugly in a circle. Approximately 7 gm. of charcoal was weighed into each dish. At the center of the desiccator was placed another dish containing an excess of carbon tetrachloride. The desiccator was evacuated slowly and carefully by means of a water pump and then allowed to stand for three hours. If kept in a draft-free location, it was found that thermostatic control was not required. If the temperature of the room varies much, it would be desirable to place the desiccator in a lagged box. After the three-hour period, dried air was slowly admitted into the desiccator through a capillary stopcock. It was noticed that some droplets of carbon tetrachloride condensed on the dishes during this operation. This was allowed to evaporate by exposing the open dishes to the air for five minutes before the lids were placed on the weighing bottles.

Weighing gave the ratios of the weight activities at saturation. With the additional determination of bulk density as described above, the ratios of the volume activities could be obtained.

It is advisable to use three samples of each charcoal and so obtain an average ratio for two charcoals against the standard. By using several desiccators many samples can be compared in the course of a day by this method.

The procedure suggested above has the greatest value for charcoals that have been activated in the same manner and have isotherms of similar shapes. Charcoals that have greatly differing isotherms will give different results between the flow method and the isopiestic method unless a very long charcoal column is used in the former (e.g., charcoal No. 1). In any case, the behavior of the charcoal at low partial pressures of the adsorbed vapor may be ascertained by obtaining isopiestic ratios at these low pressures in addition to the saturation values. If the charcoal is to be used under static conditions, the isopiestic saturation values would appear to be more meaningful than the standard flow method *V.A.*'s, which have such great dependence on the conditions of measurement.

Sorption of Other Vapors

The investigation was extended to include the determination of the isopiestic saturation value for water, amyl chloride, benzene, methyl alcohol, *n*-hexane, mustard gas, and phosgene in addition to the original carbon tetrachloride results. For the first five of these the same procedure was used to obtain equilibrium at saturation as for carbon tetrachloride, the time necessary varying from 2 to 48 hr., the actual time depending on the volatility of the liquid used.

In the case of mustard gas, which has a very low volatility, an attempt was made to expose more liquid surface by using a larger dish, but even then equilibrium was reached only after two weeks. With two samples of charcoal present instead of eight, equilibrium was attained in four to five days. Thus the charcoals adsorb the material very quickly, the lengthy time necessary being entirely due to the slow rate of evaporation of the liquid.

With phosgene, a gas at room temperature, it was necessary to modify the procedure somewhat. The phosgene tank was connected to a 2-liter bulb, then to a mercury manometer and the desiccator containing the charcoal samples. The system was completely evacuated and then phosgene was slowly admitted until the pressure was about 70 cm. More phosgene was allowed in as the mercury level changed until equilibrium was reached, indicated by no further movement of the mercury.

The experimental results are given in Table IV. Taking charcoal No. 7 as standard, the ratios of the isopiestic *V.A.*'s for each sample against that for No. 7 are given in Table V for the various vapors. The ratios for the different

TABLE IV
ISOPIESTIC SATURATION VALUES FOR VARIOUS VAPORS

Vapor	Gm. adsorbed/100 cc. for charcoal No.:				
	1	2	3	7	9
Carbon tetrachloride	26.2	24.4	30.2	38.2	39.4
Phosgene	24.3	20.6	28.2	33.5	34.0
Mustard gas	21.8	19.8	25.7	31.9	32.9
Water	15.9	14.1	18.9	23.0	
Amyl chloride			18.0	22.6	
Benzene	15.5	13.6	17.3	22.0	
Methyl alcohol	13.5	12.0	15.7	19.5	
<i>n</i> -Hexane			13.3	16.8	

TABLE V
ISOPIESTIC RATIOS FOR VARIOUS VAPORS

Vapor	Ratios to No. 7 for charcoal No.:			
	1	2	3	9
Carbon tetrachloride	0.686	0.638	0.790	1.030
Phosgene	0.725	0.615	0.842	1.015
Mustard gas	0.683	0.621	0.805	1.032
Water	0.692	0.613	0.823	
Amyl chloride			0.797	
Benzene	0.705	0.618	0.787	
Methyl alcohol	0.692	0.615	0.805	
<i>n</i> -Hexane			0.792	
Average	0.697	0.620	0.805	1.026
Supplier's <i>V.A.</i> ratios	0.620	0.643	0.836	1.107

vapors appear to be the same for each charcoal sample, taking into consideration the nonuniformity of the charcoal, so that any one of the liquids could serve as a medium for the activity test at saturation.

To illustrate the latter point further, the specific gravities of the various liquids used were measured at room temperature (24° to 25° C.) and the weights of adsorbed material converted into volumes. These values are given in Table VI.

With the exception of water, the liquid volumes are very uniform for each charcoal sample and show agreement with the rule given by McBain (6): "Equal volumes of different vapours, measured in the form of the corresponding liquids are sorbed by a given charcoal when P is approaching P_s ". Water, however, gives a lower volume in each case. This indicates that the simple picture of capillary condensation cannot be used to explain this phenomenon.

TABLE VI
LIQUID VOLUMES ADSORBED

Vapor	Liquid specific gravity	Cc. of corresponding liquid adsorbed per 100 cc. of charcoal No.:				
		1	2	3	7	9
Carbon tetrachloride	1.58	16.6	15.4	19.1	24.2	24.9
Phosgene	(1.39)*	17.5	14.8	20.3	24.1	24.5
Mustard gas	1.27	17.2	15.6	20.1	25.1	25.9
Water	1.00	15.9	14.1	18.9	23.0	
Amyl chloride	0.880			20.4	25.7	
Benzene	0.876	17.7	15.5	19.8	25.1	
Methyl alcohol	0.792	17.1	15.2	19.8	24.6	
n-Hexane	0.660			20.2	25.4	
Average		17.0	15.1	19.8	24.6	25.1

* *International Critical Tables* (4).

Acknowledgments

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n-EICOS-11-ENOIC ACID¹

BY C. Y. HOPKINS, MARY J. CHISHOLM, AND JOHN HARRIS

Abstract

Natural sources of *cis-n*-eicos-11-enoic acid, a convenient method of isolating the acid, and its conversion to the *trans*-form are described. It was found that the principal eicosenoic acid of a sample of Atlantic cod liver oil (*Gadus callarias*) was the Δ^{11} isomer, in contrast to the reports of other workers who investigated Pacific codfish and found only the Δ^9 isomer. The following derivatives are reported: *cis-n*-eicos-11-enoic anilide, N-hydroxyamide, epoxide, chlorohydrin; 11,12-dihydroxyeicosanoic acid (low-melting isomer), and its amide; *trans-n*-eicos-11-enoic acid, its hydrazide, and N-hydroxyamide. Some new physical constants of the *cis*-acid and its methyl ester are given.

Relatively little is known of the eicosenoic acids, $C_{20}H_{38}O_2$, although the neighboring acids of the even-numbered series, oleic and erucic, have been studied in considerable detail. Discovery of good sources of *cis-n*-eicos-11-enoic acid provided an opportunity for further investigation of this substance and its derivatives.*

Eicosenoic acid has been isolated from a number of marine animal oils and fish oils, especially cod liver oil (3), and from jojoba seed (7, 13), hare's-ear mustard seed (12), and rapeseed (6). A small amount of the acid has been found in hog fat (16) and some evidence of its presence has been noted in various seed fats such as those of *Nephelium lappaceum* L. (11), *Erythrina Crista-Galli* L. (4), and *Lophira alata* Banks (15). The Δ^{11} isomer has been prepared artificially by degradation of erucic acid (2) and by condensation of oleyl bromide with malonic ester (22).

Two forms of eicosenoic acid have been reported in nature: Δ^9 and Δ^{11} . Eicosenoic acid from plant sources so far examined has been shown to be eicos-11-enoic acid (7, 12). The acid from hog fat was the same (16).

Among the oils of marine fauna, the Δ^{11} isomer has been reported in menhaden body oil by Baldwin and Parks (1) and in cod liver oil by Vesely and Chudozilov (22).

The usual form in marine oils, according to Japanese workers, is eicos-9-enoic acid. Evidence for the Δ^9 structure was obtained by ozonolysis experiments (18, 21). Takano and Toyama and coworkers concluded thereby that cod liver, Japanese sardine, and herring oils contained eicos-9-enoic acid. Thus there is disagreement as to whether the eicosenoic acid of cod liver oil has the Δ^9 or Δ^{11} structure.

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* The natural acid is presumed to be the *cis*-form by analogy with oleic acid, i.e., assuming that the lower melting form has the *cis*-configuration.

Vesely and Chudozilov prepared *cis*- and *trans*-eicos-11-enoic acid from oleyl bromide by condensation with malonic ester. They compared derivatives of the *cis*-acid with those of natural eicosenoic acid from cod liver oil and concluded that they were identical.

Results and Discussion

Specimens of eicosenoic acid were prepared during the present investigation from jojoba seed (*Simmondsia californica* Nuttall), hare's-ear mustard seed (*Conringia orientalis* L.), and cod liver oil (Atlantic codfish, *Gadus callarias*).

Jojoba seed is the most convenient source. Care must be taken to remove completely the long-chain alcohols which are not easy to separate from the fatty acids by the ordinary procedures. A method is described in the experimental part.

It has been shown by oxidation with permanganate in acetone that the eicosenoic acid of jojoba seed has the Δ^{11} structure (7). Similarly, it has been proved by periodate oxidation that the acid from *Conringia orientalis* L. is the Δ^{11} form (12).

In the present work, a very careful purification of eicosenoic acid from cod liver oil was made and the product was compared with pure eicos-11-enoic acid from jojoba seed by means of suitable derivatives. The results provide conclusive evidence that our specimen of eicosenoic acid from cod liver oil is eicos-11-enoic acid (Table I).

TABLE I
MELTING POINT OF DERIVATIVES, °C.

Substance	From cod liver oil	From jojoba seed	Mixed
11,12-Dihydroxyeicosanoic acid (by H_2O_2)	94-95.5	95-96	94.5-96
11,12-Dihydroxyeicosanoic acid (by $KMnO_4$)	129-130	129-130	129-130
<i>cis</i> -Eicos-11-enoic acid N-hydroxyamide	67-68	69-70	68-69

The two isomeric dihydroxy derivatives of the acid are analogous to the two dihydroxystearic acids prepared from oleic acid in similar manner.

For further proof of structure, the dihydroxyeicosanoic acid from cod liver oil, m.p. 94° to 95.5° C., was subjected to periodate oxidation and the products were identified as 10-aldehydo-decanoic acid and nonaldehyde (Table II). The original substance must therefore be *n*-eicos-11-enoic acid.

Derivatives of the cod liver oil acid were a little more difficult to purify than those of the jojoba acid.

TABLE II
MELTING POINT OF CLEAVAGE PRODUCTS, °C.

Substance	From cod liver oil	From jojoba seed	Mixed
10-Aldehydo-decanoic acid semicarbazone	161-162*	161-162	161-162
Nonaldehyde semicarbazone	94-95	96-97	95-97

* Mixed melting points with 8-aldehydo-octioic acid semicarbazone and with 12-aldehydo-dodecanoic acid semicarbazone showed a depression of about 10° C. in each case.

The occurrence of eicosenoic acids in marine fauna is summarized in Table III.

TABLE III
EICOSENOIC ACIDS IN MARINE FAUNA

Source	Reference	Isomer reported	M.p. of acid, °C.	M.p. of dihydroxy derivative (by KMnO ₄), °C.
Cod liver oil ("Lofoden")	3	—	24.5	127.5 to 128
Cod liver oil	22	Δ ¹¹	23 to 24	—
Cod liver oil	21	Δ ⁹	24 to 24.5	—
Japanese sardine	18	Δ ⁹	22 to 23	—
Japanese sardine	21	Δ ⁹	24 to 24.5	128 to 128.5
Pilot whale (<i>Globiocephalus sieboldii</i> Gray)	20	—	23.5 to 24	126.5 to 127*
Sperm whale	10	—	—	—
Menhaden (<i>Brevoortia tyrannus</i>)	1	Δ ¹¹	—	115.5 to 116**
Menhaden (<i>Brevoortia tyrannus</i>)	17	—	—	129.2 to 129.5
Cod liver oil (<i>Gadus callarias</i>)	Present work	Δ ¹¹	20.5	129 to 130

* Marked lowering of melting point reported with 9,10-dihydroxy acid.

** Admittedly impure.

A carefully purified sample of *cis*-eicos-11-enoic acid from jojoba seed (m.p. 22° C.) had refractive index $n_D^{20} = 1.4616$, $n_D^{25} = 1.4600$.

Purified samples of methyl *cis*-eicos-11-enoate from jojoba seed and from cod liver oil had refractive index $n_D^{20} = 1.4550$; $n_D^{25} = 1.4531$. The ester melts at about -15° C.

Few derivatives of eicos-11-enoic acid are known. Derivatives prepared during the present work are listed in Table IV.

TABLE IV
DERIVATIVES OF *n*-EICOS-11-ENOIC ACID

Compound	M.p., °C.	Formula	Analysis, %
<i>cis</i> -Eicos-11-enoic amide	79–80*	C ₂₀ H ₃₉ ON	{ Found: N, 4.5, 4.4 Calc.: N, 4.5
<i>cis</i> -Eicos-11-enoic anilide	51–52.	C ₂₈ H ₄₅ ON	{ Found: N, 3.5, 3.5 Calc.: N, 3.6
<i>cis</i> -Eicos-11-enoic N-hydroxy- amide	69–70	C ₂₀ H ₃₉ O ₂ N	{ Found: N, 4.5 Calc.: N, 4.3
11,12-Epoxyeicosanoic acid	55.0–55.5	C ₂₀ H ₃₈ O ₃	{ Found: C, 73.2; H, 11.4 Calc.: C, 73.6; H, 11.7
11,12-Dihydroxyeicosanoic acid, low m.p. isomer	95–96	C ₂₀ H ₄₀ O ₄	{ Found: C, 69.8; H, 11.5 Calc.: C, 69.7; H, 11.7
11,12-Dihydroxyeicosanoic amide, low m.p. isomer	116–117	C ₂₀ H ₄₁ O ₃ N	{ Found: N, 4.1, 4.2 Calc.: N, 4.1
Chlorohydrin of eicos-11-enoic acid	39–40	C ₂₀ H ₃₉ O ₃ Cl	{ Found: Cl, 9.92 Calc.: Cl, 9.77
<i>trans</i> -Eicos-11-enoic acid	52–53**	C ₂₀ H ₃₈ O ₂	{ Found: Equiv. 311, 312 Calc.: Equiv. 310.5
<i>trans</i> -Eicos-11-enoic N-hyd- roxyamide	93–94	C ₂₀ H ₃₉ O ₂ N	{ Found: N, 4.2, 4.4 Calc.: N, 4.3
<i>trans</i> -Eicos-11-enoic hydrazide	103	C ₂₀ H ₄₀ ON ₂	{ Found: N, 8.4, 8.4 Calc.: N, 8.6

* Vesely, 78° to 79° C. (22).

** Vesely, 53° to 54° C.

trans-Eicos-11-enoic acid has previously been prepared by partial synthesis. Bodenstein reported a melting point of 50° C. (2) and Vesely and Chudozilov found it to be 53° to 54° C. (22).

The eicosenoic acid from Japanese sardine oil (reported to be the Δ^9 isomer), when converted to the *trans*-form, melted at 51.5 to 52° C. (21).

Experimental

Isolation of Eicosenoic Acid from Jojoba Seed

A quantity of *cis*-eicos-11-enoic acid was isolated from jojoba seeds.* The procedure differed from that of Green, Hilditch, and Stainsby in the method of removing the long-chain alcohols.

The liquid wax (350 gm.) was saponified with ethanolic potassium hydroxide, and after distilling off most of the ethanol, the mixture was dried on the steam bath to a paste. The paste was leached with several portions of

* Kindly furnished by Mr. Frederick Gibson.

acetone and the undissolved soaps were extracted further with acetone in the Soxhlet. Finally the acetone was replaced by ether and the extraction was continued for several hours.

The residual soaps were boiled with excess 1:1 hydrochloric acid in the presence of chloroform. The chloroform layer was separated off. It yielded the free fatty acids upon removal of the solvent.

The mixed fatty acids were converted to methyl esters and these were fractionally distilled in the usual way. The three main fractions had iodine values 79.1, 78.1, 77.4 respectively (methyl eicosenoate: 78.4). It is estimated from the fractionation data that eicosenoic acid constitutes at least 60% of the total fatty acids of the seed and that the content of docosenoic acid is not more than 25%. These figures correspond fairly well with those of McKinney and Jamieson (13).

The methyl eicosenoate was recrystallized from acetone (10 ml. per gm.) at -40°C . The product had iodine number 78.4 (theory 78.4). A portion was hydrolyzed to the acid and the acid was recrystallized from acetone at -15°C . It had iodine number 81.4 (theory, 81.8). The melting point was 22°C . when determined by the open capillary tube method described by Hilditch (9). The setting point (titer) was 21° to 22°C .

Isolation from Cod Liver Oil

A specimen of cod liver oil from the species *Gadus callarias* (North Atlantic) was kindly supplied by Dr. S. A. Beatty. The oil (iodine number, 156) was converted to methyl esters in 600 gm. lots and these were fractionally distilled in the usual way at a pressure of less than 1 mm. The distillation curve showed flattened portions corresponding to the boiling points of C_{16} , C_{18} , and C_{20} esters. The C_{20} fraction was subjected to fractional crystallization from acetone at low temperatures (10 ml. per gm.). The product, methyl eicosenoate, had iodine number 78.7 (theory, 78.4). The free acid obtained therefrom melted at 20.5°C . The compounds listed in Tables I and II were prepared from this acid.

Isolation of the acid from hare's-ear mustard seed (*Conringia orientalis* L.) has already been described (12).

The acid obtained from jojoba seed was used for the preparation of derivatives listed in Table IV.

cis-Eicos-11-enoic Amide and Anilide

The acid chloride was readily prepared by allowing the free acid to stand overnight with phosphorus trichloride. On treating the acid chloride with ammonia, the amide was precipitated. It was recrystallized from ethyl acetate. The anilide, prepared in the same way, was recrystallized from acetone.

cis-Eicos-11-enoic N-Hydroxyamide

Methyl eicosenoate and hydroxylamine were reacted in alkaline solution according to the general method of Renfrow and Hauser (14). The potassium salt, which precipitated slowly, was filtered off and acidified cautiously. The N-hydroxyamide was recrystallized several times from acetone.

11,12-Epoxyeicosanoic Acid

cis-Eicos-11-enoic acid was converted to the epoxy compound by the general method of Findley, Swern, and Scanlan (5) using peracetic acid. The product was recrystallized successively from petroleum ether, acetone, and methanol. It is slightly soluble in petroleum ether but readily soluble in ethanol, benzene, and chloroform.

11(or 12)-Chloro-12(or 11)-hydroxyeicosanoic Acid

The epoxy acid was treated with dry hydrogen chloride in dry ether. After four crystallizations from petroleum ether the product melted at 39° to 40°. It is readily soluble in ethanol, benzene, acetone, and chloroform.

11,12-Dihydroxyeicosanoic Acid

The low-melting isomer, prepared by the action of hydrogen peroxide on eicosenoic acid, was prepared earlier (12). The melting point and analysis are given in Table IV. The high-melting isomer, m.p. 130° C., is well known.

11,12-Dihydroxyeicosanoic Amide

The low-melting isomer was prepared by the action of hydrogen peroxide on eicosenoic amide in the presence of formic acid. The product was recrystallized from ethyl acetate.

trans-Eicos-11-enoic acid

Isomerization of the *cis*- to the *trans*-acid was effected readily by means of Poutet's reagent, using the procedure of Griffiths and Hilditch (8) as follows.

One part of the reagent (6 gm. mercury dissolved in 15.6 ml. nitric acid, *d* 1.42) is added to 12 parts of the eicosenoic acid and the mixture is immediately cooled under the tap with vigorous shaking. It is allowed to stand for several hours and is then recrystallized from ethanol.

trans-Eicos-11-enoic N-Hydroxyamide

A specimen of *trans*-eicos-11-enoic acid was esterified with methanol via the acid chloride. The ester was treated with hydroxylamine by the procedure of Renfrow and Hauser (14) and the product was recrystallized twice from ethanol. It appeared to contain some dihydroxy amide. The desired product was obtained by warming with toluene, in which it is soluble, and filtering off the impurity. The N-hydroxyamide was isolated as lustrous white flakes, somewhat soluble in toluene and ethanol, but insoluble in water.

trans-Eicos-11-enoic Hydrazide

Methyl *trans*-eicos-11-enoate (3 gm.) was mixed with 3 ml. of hydrazine hydrate (85% solution) in 30 ml. of absolute ethanol. The mixture was refluxed on the steam bath for two hours, cooled in ice, and the crystalline product was filtered off. It was purified by washing with hexane and recrystallizing three times from toluene.

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ON THE MECHANISM OF OXIDATION OF *trans*-DECAHYDRONAPHTHALENE AT 100° C.¹ MAY 1949

BY D. S. McARTHUR AND E. A. SMITH

Abstract

The mechanism of oxidation of the *trans*-isomer of decahydronaphthalene (*trans*-decalin) by gaseous oxygen at 100° C. has been studied. The rate of retention of oxygen by decalin and the rates of formation of three volatile oxidation products were measured over the first 100 to 200 hr. of the oxidation reaction. The rate of retention of oxygen has been found to be independent of the oxygen concentration in the oxidizing gases but to depend on decalin concentration to the three-halves power. The rates of formation of the volatile oxidation products are also independent of oxygen concentration but are proportional to the decalin concentration. The activation energies of each of the reactions were determined. An initiating reaction forming carbon monoxide and hydrogen has been postulated based on the ratio of the rates of formation of the volatile compounds in the inhibited period of oxidation. Some data on the mechanism of the oxidation reaction in the accelerated period have also been obtained.

Introduction

The mechanism of oxidation of decalin (decahydronaphthalene) by gaseous oxygen at 100° C. has never been elucidated. Balsbaugh and Oncley (1) oxidized decalin at 75° C. and found that peroxides were formed almost exclusively in the initial period. Larsen *et al.* (15) oxidized decalin at 110° C. and determined the amount of saponifiable material, acids, etc., among the oxidation products. Ivanov and Savinova (10) oxidized decalin at 70° C. under the influence of ultraviolet light and found that the hydroperoxide was formed. However, no attempt was made by these authors to determine the actual mechanism of the oxidation reaction.

In this work the *trans*-isomer of decalin was oxidized at 100° C. The rate of oxygen uptake by the decalin and the rates of formation of three volatile oxidation products were followed as the oxidation progressed. It was possible to determine the effect of temperature, the effect of decalin concentration, and the effect of oxygen concentration in the oxidizing gases on the oxidation reaction. The data obtained give some insight into the mechanism of the oxidation reaction in the initial stages. Some evidence of the type of mechanism accounting for oxygen uptake in the accelerated period was also obtained from a partial analysis of the oxidation products formed in the decalin.

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.

Experimental

Epilome

Samples of 100 ml. of decalin were held at 100° C. and subjected to oxidation by the passage of a continuous stream of oxygen in a closed circuit. The volatile oxidation products were absorbed from the oxygen stream and determined by periodic weighing of the absorbers. The total oxygen flow into the closed circuit was measured and recorded automatically. The oxygen absorbed and retained by the decalin was determined from the difference between the total oxygen consumed in the circuit, as recorded automatically, and the oxygen collected with the volatile oxidation products as determined from the absorbed weights.

The effect of temperature on the reaction was determined by making oxidation runs at temperatures ranging from 80° to 120° C. The effect of decalin concentration was determined by oxidizing solutions of decalin in silicone fluid, and the effect of oxygen concentration was determined by oxidizing the decalin with oxygen diluted with nitrogen.

The Oxidation Apparatus

The oxidation apparatus used was patterned after that used by Fenske *et al.* (6). It consisted essentially of two parts, a circulating system in which oxygen was circulated continuously through the decalin sample by means of a glass-mercury pump (12), and an inlet line that maintained a constant, positive oxygen pressure (5 mm. mercury over atmospheric) on the circulating system and that measured and recorded the amount of oxygen flowing into the circulating system.

The pump drew oxygen from a reservoir and forced it through a buffer and flowmeter into the decalin sample. The oxygen stream bubbled through the sample and passed on, carrying with it the volatile oxidation products formed and a little vaporized decalin. The stream passed through a Graham condenser (which condensed out part of the decalin vapor) and through water and carbon dioxide absorbers where water formed by the oxidation reaction was removed. (It was found that no carbon dioxide was formed.) The oxygen stream then passed into a cold trap held at -70° to -80° C. where the remainder of the decalin vapor in the oxygen stream was trapped out. Any compounds sufficiently volatile to pass through the cold trap were ignited in a combustion furnace and the water and carbon dioxide formed were absorbed before the oxygen returned to the reservoir for recirculation. The hydrogen and carbon-bearing compounds ignited in the furnace were called "volatile hydrogen" and "volatile carbon" compounds respectively.

As oxygen was consumed in the circulating system, more passed in through the inlet line. The amount passing in was measured and recorded automatically by a wetmeter and oxygen-recorder system so that a continuous record of the oxygen consumed in the circulating system was kept as the oxidation run progressed.

That portion of the total oxygen consumed that was combined with the volatile oxidation products was determined by periodic weighings of the absorbers. Two parallel sets of absorbers were supplied so that the oxidation run did not have to be interrupted. Analysis of the small amounts of decalin (0 to 3 ml. in 100 hr.) trapped out from the oxygen stream indicated that no oxygenated compounds were removed with the decalin vapor. The portion of the total oxygen consumed that was absorbed and retained by the decalin could therefore be determined by difference.

It was found convenient to base all calculations on the moles of oxygen reacted or combined per liter of liquid sample being oxidized, and the results are reported in this form. Reaction rates are reported in moles of oxygen reacted per liter of sample per hour.

Chemicals

The *trans*-isomer or decahydronaphthalene (*trans*-decalin) was used in this work. It was obtained from commercial decalin. The decalin was first thoroughly acid-treated to remove aromatic and unsaturated compounds, shaken with ferrous sulphate to remove peroxides and dried over sodium hydroxide. The *trans*-isomer was then separated from the mixture by slow distillation at 10 to 12 mm. pressure through a Stedman column. The properties of the resultant product checked with those reported in the literature for *trans*-decalin.

The silicone fluid that was used as a diluent for the decalin was silicone fluid DC-550 as supplied by Fiberglas Canada Ltd. It absorbs oxygen at a low linear rate and forms water also at a low linear rate. However, since the rates are small compared to that for decalin, corrections could readily be made. It was found to be chemically inert in its effect on the rate of oxygen retention in decalin and on the rate of formation of water in the oxidation reaction.

Results

Under the conditions described, in which oxygen was bubbled through the decalin at 100° C. and recirculated after absorption of the water and removal of the volatile hydrogen and carbon compounds, it was found that about 81% of the total oxygen consumed in the circuit during the first 100 hr. is absorbed and retained by the decalin. Some preliminary work on the oxidized decalin indicated that this oxygen is divided with about half of it in the form of peroxides and a large part of the remainder in the form of hydroxy compounds and a small part (1 to 2%) in the form of an insoluble (in decalin) acid, 1-cyclohexene-1,2-dicarboxylic acid. About 13% of the total oxygen consumed reacts with the decalin to form water, which passes out of the reaction chamber with the oxygen stream as water vapor and is absorbed. The remainder of the oxygen consumed (about 6%) is combined with the volatile hydrogen and carbon compounds after their combustion to form water and carbon dioxide. The effects of temperature, decalin concentration, and oxygen concentration on these reactions are discussed in the following sections.

(a) The Oxidation Reaction at 100° C.

Each of the four reactions progressing simultaneously during the oxidation were studied:

- (1) The reaction by which oxygen was absorbed and retained in the decalin,
- (2) The reaction by which water was formed as a volatile oxidation product,
- (3) The reaction forming volatile carbon compounds, and
- (4) The reaction forming volatile hydrogen.

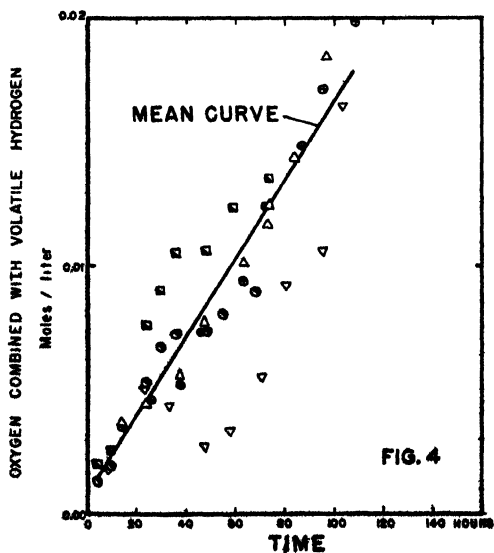
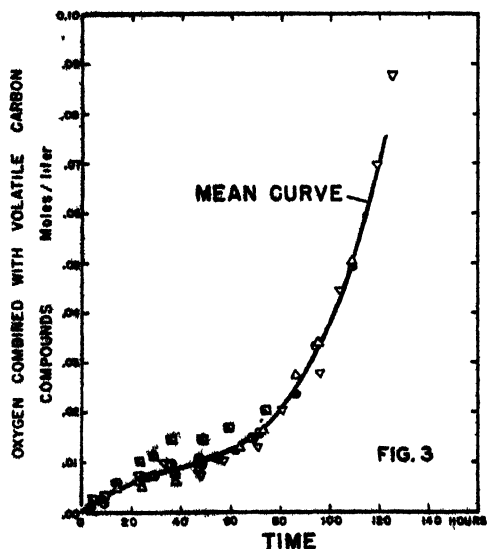
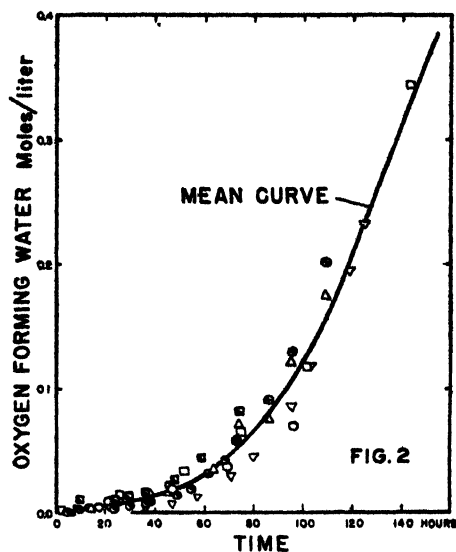
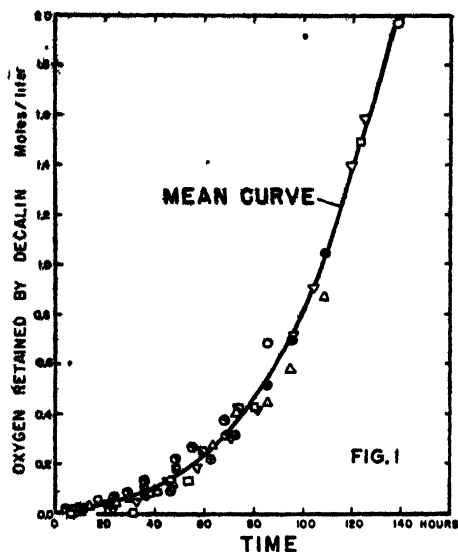


FIG. 1. Oxygen retained by decalin with time. Each set of symbols represents a separate test oxidation run.

FIG. 2. Oxygen combined to form water.

FIG. 3. Oxygen combined with volatile carbon compounds.

FIG. 4. Oxygen combined with volatile hydrogen.

The oxygen reacted or combined in each reaction is shown plotted against time in Figs. 1, 2, 3 and 4. It was found that no carbon dioxide is formed as an oxidation product during the first 100 hr. of the oxidation reaction. Fig. 1 shows that the decalin absorbs oxygen slowly at first with a gradual acceleration in the rate of absorption. A constant rate of about 360×10^{-4} mole of oxygen per liter per hr. is reached at 120 hr. as shown in Table I.

TABLE I

DATA ON THE OXIDATION REACTION AT 100° C.

Reaction	Reaction rates, moles O ₂ /liter/hr. $\times 10^4$		Activation energy, kcal./mole		Effect of decalin concentration [D] on reaction rate		Effect of oxygen concentration on reaction rate	
	Initial	Accel- erated	Initial	Accel- erated	Initial	Accel- erated	Initial	Accel- erated
Oxygen retention	—	361.3	23.0	23.0	None	15.7[D] ^{1/2}	None	None
Formation of water	3.22	51.2	5.6	7.6	None	8.20[D]	None	None
Formation of volatile carbon compounds	2.09	25.0	10.2	20.7	1.44[D]	2.58[D]	None	None
Formation of volatile hydrogen	1.58	—	7.0	—	0.53[D]	—	None	—

The exact value for the initial rate of oxygen retention could not be determined.

Fig. 2 shows the absorption of oxygen by the water-forming reaction with time. The rate of water formation was found to be relatively constant at 3.2×10^{-4} mole oxygen per liter per hr. for 30 to 40 hr. followed by gradual acceleration to a steady-state rate of 51.2×10^{-4} mole oxygen per liter per hr. at about 120 hr. as shown in Table I.

Fig. 3 shows the oxygen combined with volatile carbon compounds plotted against time. The rate of formation of volatile carbon compounds is relatively constant over the first 60 hr. of oxidation at 2.1×10^{-4} mole oxygen per liter per hr. but then accelerates to about 25.0×10^{-4} mole oxygen per liter per hr.

Fig. 4 shows the formation of volatile hydrogen in terms of the oxygen combined with it to form water. The rate of formation is constant at 1.6×10^{-4} mole oxygen per liter per hr. throughout the entire period studied.

The idealized changes in the reaction rates with time as determined from the slope of the oxygen-reacted versus time curves are shown in Fig. 5.

(b) The Effect of Temperature on the Oxidation Reaction

The activation energy of each of the reactions was determined in both the initial and the accelerated period and these results are also shown in Table I.

In determining the activation energy the decalin concentration was assumed to be constant (pure decalin) throughout the run since only a small proportion of the decalin is oxidized during the initial oxidation period studied. The

oxygen concentration in the oxidizing medium was also held constant at 100% oxygen for these tests. The rate equation can therefore be simplified from:

$$\text{Rate} = K[\text{O}_2]^\alpha [\text{D}]^\beta$$

where

$[\text{O}_2]$ = oxygen concentration (constant),

$[\text{D}]$ = decalin concentration (constant),

α and β are constants

to

$$\text{Rate} = K \times \text{constant}$$

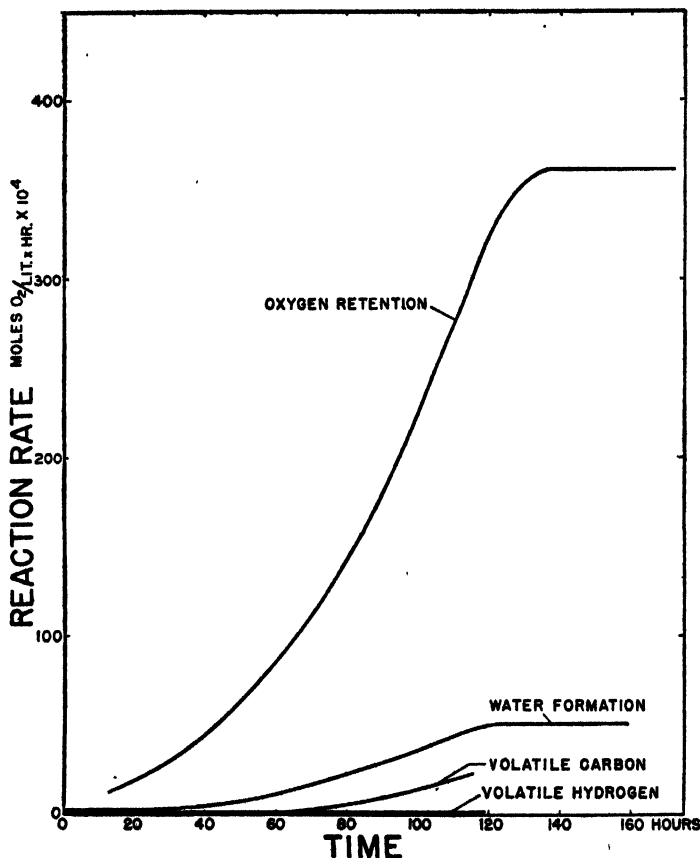


FIG. 5. The change in reaction rates with time.

The activation energy was determined from the slope of the plot of $\ln(K \times \text{constant})$ against $1/T$, where T is the absolute temperature.

In the case of the oxygen-retention reaction the reaction rates in the inhibited period were assumed to be inversely proportional to the length of the inhibited period as determined by projecting the accelerated absorption curve back to the time scale. In all other cases the reaction rates were determined directly from the slope of the oxygen reacted vs. time curves.

The results suggest that the same reaction accounts for oxygen retention in the decalin in both the initial and the accelerated period since the activation

energies in both cases are the same, 23.0 kcal. per mole. Water formation is by a reaction having a low activation energy (5 to 8 kcal. per mole) in both periods. Volatile carbon compounds are formed by a reaction having an activation energy of 10.2 kcal. per mole in the initial period (first 60 hr.) and by a reaction having an activation energy of 20.7 kcal. per mole in the accelerated period. Volatile hydrogen formation is by a reaction having a low activation energy (about 7.0 kcal. per mole) throughout the period studied.

(c) *The Effect of Decalin Concentration*

The effect of decalin concentration on the oxidation reaction was determined by making oxidation runs with varying proportions of decalin dissolved in the chemically inert silicone fluid.

The results obtained are also shown in Table I. There is no measurable effect of decalin concentration on the oxygen-retention reaction nor on the water-forming reaction in the initial stages. The oxygen-retention reaction however is quite sensitive to decalin concentration in the accelerated period, the rate being proportional to decalin concentration to the three-halves power as shown. All the other reaction rates are proportional to decalin concentration and differ only in the proportionality factors.

The silicone fluid catalyzes the initial rates of formation of volatile carbon compounds and volatile hydrogen. Two per cent silicone in decalin is sufficient to increase the rate of formation of volatile carbon compounds to 3.5 times the rate in pure decalin and to increase the rate of formation of volatile hydrogen to twice the rate in pure decalin.

(d) *Effect of Oxygen Concentration*

The oxidation reaction at 100° C. is completely independent of the oxygen concentration in the oxidizing mixture. An oxidation run was made in which the oxygen concentration in nitrogen was allowed to decrease from 50% to less than 1% as the run progressed. The system was then swept out with an oxygen-nitrogen mixture containing 80% oxygen and the run continued. In spite of the wide fluctuations in oxygen concentration, the experimental points obtained fell within the experimental error on the oxidation curves obtained with 100% oxygen. It was also observed that the reaction is independent of the rate at which the oxidizing gases are pumped through the system, provided the rate is in excess of some undetermined minimum.

(e) *Oxidation Products Formed in the Decalin*

In oxidation runs at 100° C. where more than 0.1 mole of oxygen is retained per liter of decalin, a small amount of a white crystalline precipitate settles out after the decalin has stood for a day or more at room temperature. Some roughly quantitative determinations indicated that it is formed in an approximately linear manner with time and at a very low rate, about 100 mgm. being

formed in a 100 ml. sample of decalin after 100 hr. of oxidation. The precipitate can be recrystallized from benzene, forming colorless, needlelike crystals that have been identified as 1-cyclohexene-1,2-dicarboxylic acid.

Some preliminary work was done using the method developed by Larsen (14) to determine the proportion of the total oxygen retained by the decalin which is in the form of acids, alcohols and/or hydroperoxides* ("Grignard added" oxygen). It was found as shown in Fig. 6 that there is a constant ratio between the oxygen found in the two classifications as the run progresses. Seventy-five per cent of the oxygen goes to form compounds of the "Grignard evolved" type and 25% goes to form compounds of the "Grignard added" type during the period studied.

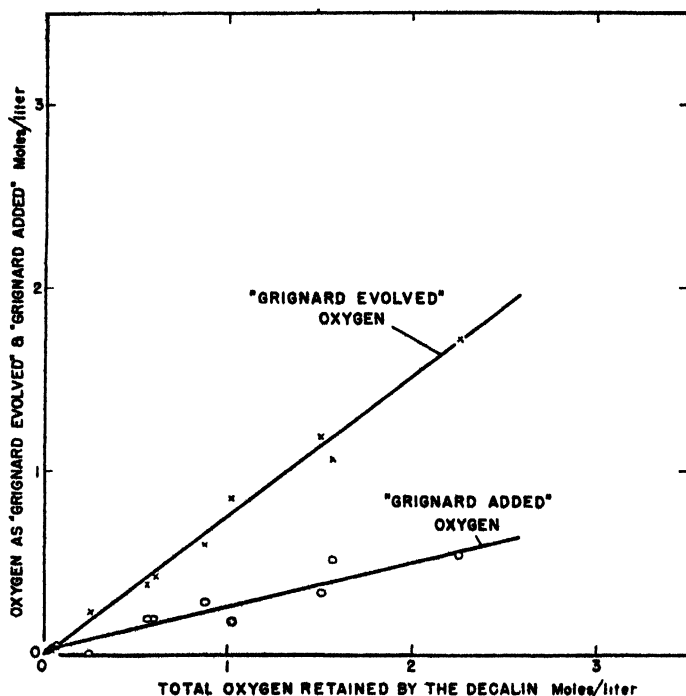


FIG. 6. Total oxygen retained by the decalin going to form "Grignard evolved" and "Grignard added" oxygen.

From quantitative tests on decalin samples drawn during the oxidation runs it was found that no carbonyl compounds are formed until 0.3 to 0.4 mole of oxygen per liter has been absorbed.

In oxidation runs where 0.8 to 1.0 mole of oxygen per liter is retained by the decalin, a viscous yellow liquid settles out. It is soluble in alcohol, acetone, acetic acid, ethyl acetate, ethyl ether, and benzene; partially soluble in decalin and carbon tetrachloride; insoluble in water, in dilute hydrochloric acid, and in dilute caustic (forming a white precipitate). It darkens with

* Hydroperoxides add one mole of Grignard and evolve one mole of methane, thus consuming two moles of Grignard reagent for each mole of the hydroperoxide.

cold concentrated sulphuric acid; reacts violently with acetyl chloride; shows no sign of unsaturation with bromine, and gives a negative test for carbonyl groups. The liquid darkens when boiled between 150° to 200° C. Analysis with Grignard reagent indicated that it contains oxygen of the "Grignard evolved" type (alcohols, acids). Elementary analysis indicated: C, 67.5; H, 9.36; O, 23.16%. It was not identified, but its chemical properties suggest that it consists largely of saturated hydroxy compounds.

Since no carbonyl compounds are present in the initial reaction stages, and from a comparison with the work of other authors (7, 8, 9, 17, 18) it seems likely that the major portion of the "Grignard added" oxygen is actually due to the presence of hydroperoxide. It follows that an equivalent amount of the "Grignard evolved" oxygen is also due to the hydroperoxide, so that approximately 50% of the oxygen retained by the decalin is present as the hydroperoxide. The saturated hydroxy compounds observed to separate out from the decalin in long oxidation runs indicate that a large part of the oxygen is also in this form.

Discussion

(a) *Initial Period of Oxidation*

As far as could be ascertained, the reaction by which oxygen is absorbed and retained by the decalin accelerates smoothly from the beginning of the oxidation, reaching a maximum steady rate of oxygen retention at 120 hr. The formation of the volatile compounds however occurs at a constant rate for the first 30 to 40 hours of the oxidation reaction. This suggests that the reaction forming the volatile compounds is an initiating reaction progressing at a constant rate and supplying radicals of a chain-initiating type which account for the smoothly accelerating rate of oxygen uptake by the decalin. After 30 to 40 hr. the formation of volatile products as a side reaction of the main oxygen-uptake reaction would account for the acceleration in the rate of formation of water and volatile carbon compounds in the later reaction.

The ratio of the rates of formation of the three volatile oxidation products during the initial 30 to 40 hr. is such that for each three molecules of water formed there are three atoms of volatile hydrogen and one atom of volatile carbon collected. The fact that the rate of formation of volatile carbon accelerates at 60 hr. without a corresponding acceleration in the rate of formation of volatile hydrogen suggests that these two elements do not come from the same compound. This conclusion is borne out by the observed differences in the activation energies of the reactions producing the two materials as shown in Table I. Moreover the ratio of the sensitivities of the reactions forming volatile hydrogen and volatile carbon compounds to decalin concentration is not as would be expected if the two elements were from the same volatile compound. In addition, although both reactions were catalyzed by the addition of 2% silicone to the decalin, the rate of formation of volatile carbon compounds was increased to 3.5 times the rate in pure decalin, whereas

the rate of formation of volatile hydrogen was only doubled. This could not be the case if the two elements were produced by the same compound. The authors were forced to conclude, therefore, that the carbon and hydrogen are actually from separate compounds.

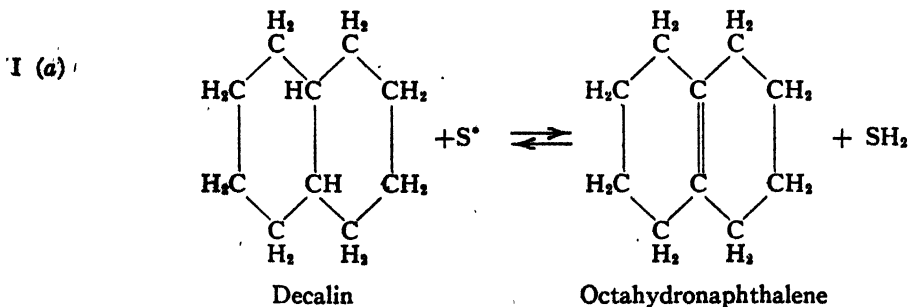
A review of the literature indicated that Kröger and Strüber (13) found carbon monoxide and hydrogen gas among the oxidation products of naphthenes. Chavanne *et al.* (2, 3, 4) reported the presence of carbon monoxide and hydrogen among the volatile oxidation products of methylcyclopentane and 1,4-dimethylcyclohexane when oxidized at 80° and 100° C. Fenske *et al.* (6) found carbon monoxide and hydrogen among the volatile oxidation products of lubricating oils and Larsen *et al.* (15) also found both gases among the oxidation products of hydrocarbons. Apparently, however, none of the authors have connected the presence of these gases with the initiating reaction.

It was assumed, therefore, that the volatile carbon compound measured is actually carbon monoxide gas and that the volatile hydrogen measured is actually hydrogen gas.

The appearance of 1-cyclohexene-1,2-dicarboxylic acid in the early stages of the reaction and its low, linear rate of formation with time suggested that it is also connected with the initiating reaction.

On this basis, the mechanism postulated for the initiating reaction involves the catalytic dehydrogenation of decalin to form octahydronaphthalene with its subsequent stepwise oxidation to 1-cyclohexene-1,2-dicarboxylic acid. The mechanism postulated produces water, carbon monoxide, and hydrogen gas in the observed ratios and accounts for the formation of decalin radicals which could initiate the oxygen-uptake reaction as shown later.

The first step postulated is the simple dehydrogenation of decalin catalyzed by the surface of the vessel:



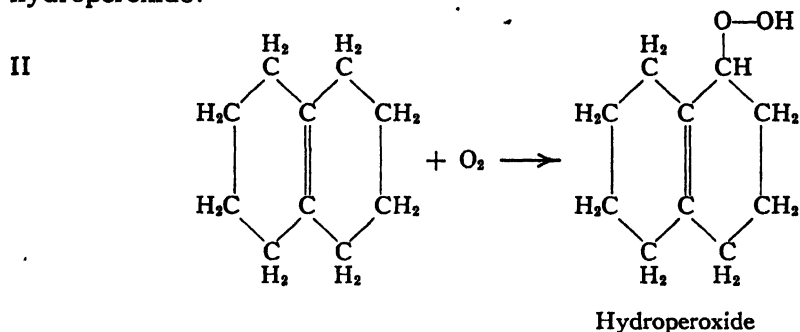
with the subsequent liberation of gaseous hydrogen:



This reaction occurs to a limited extent only. It is in accordance with the primary dehydrogenation theory postulated by Lewis (16). Waters (18) also postulates that the initial step in oxidation is the abstraction of neutral

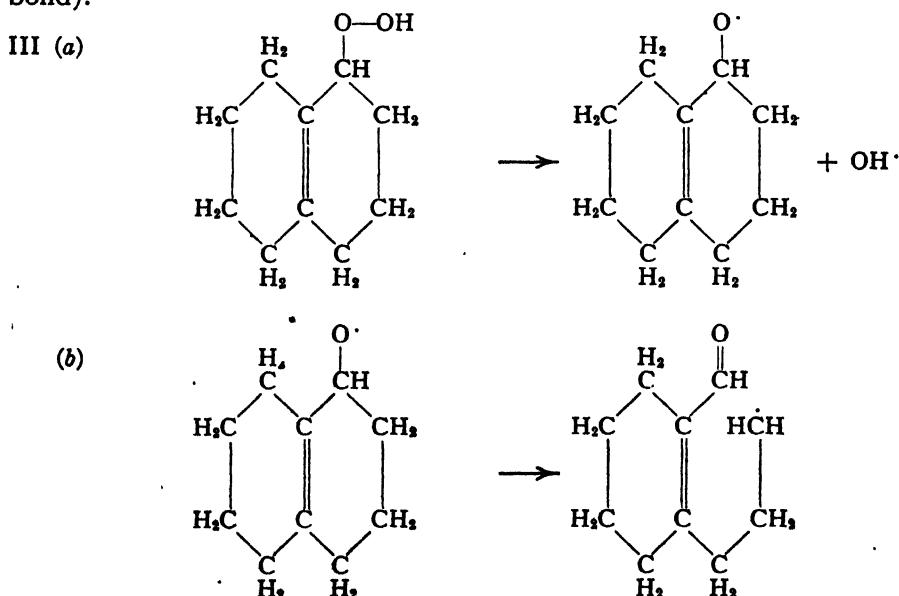
hydrogen. George and Robertson (7, 8) have shown that where no unsaturation exists, such as in decalin, the most labile hydrogen is that which is connected to a tertiary carbon atom. This would account for the abstraction of the two hydrogens from the tertiary carbon atoms.

The octahydronaphthalene formed is sensitive to oxidation, forming the hydroperoxide:

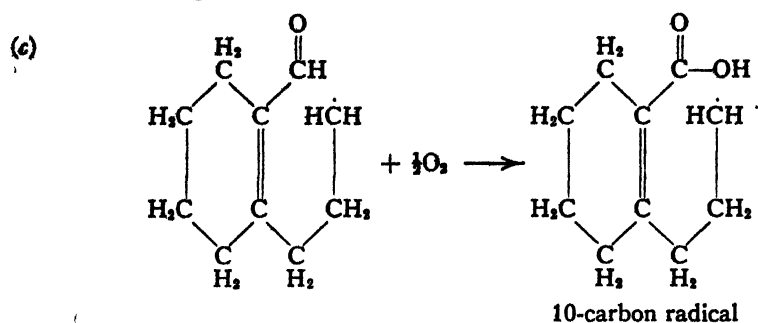


The suggested formation of the hydroperoxide on the α -position to the double bond is in accordance with the work of Farmer (5), who shows that the mechanism of addition of oxygen to an olefinic linkage is mainly by addition at the α -methyl carbon and not directly at the double bond, as frequently postulated. George and Robertson (7, 8) have also shown that the most likely point of attack by oxygen is at the weakest C—H link, which is on the carbon in the α -position to the double bond.

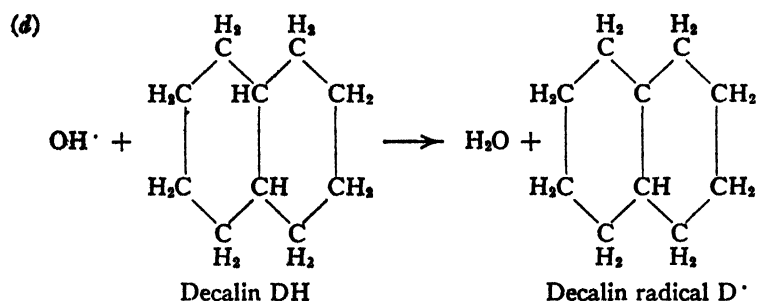
The hydroperoxide formed is unstable and decomposes by the mechanism postulated by George and Walsh (9), with splitting first at the O—O bond and then at the weakest adjacent bond of the α -carbon (other than the C—O bond).



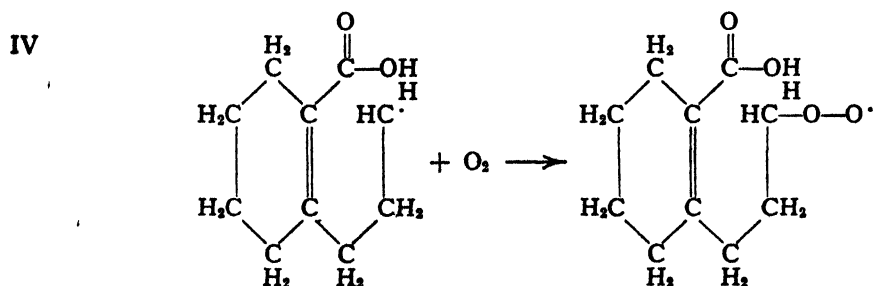
The aldehyde tip readily oxidizes to form the acid:



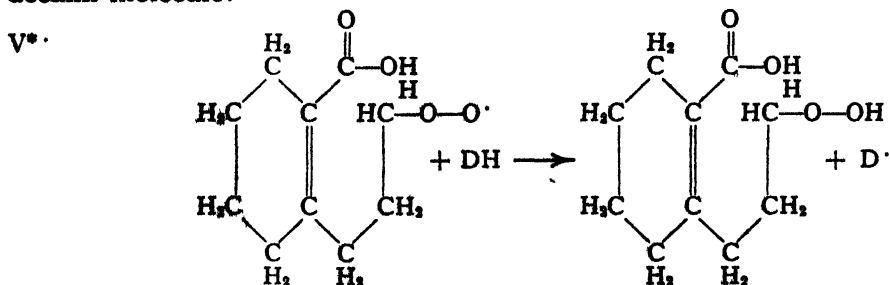
The hydroxyl group formed by Reaction III(a) can react with a molecule of decalin to form water and a decalin radical:



The active 10-carbon radical from III(c) combines with oxygen to form the hydroperoxide radical as follows:



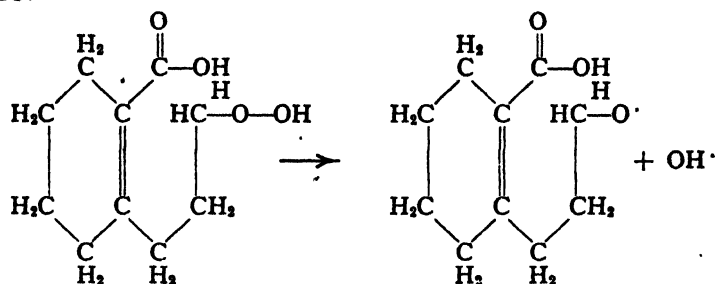
The hydroperoxide radical is capable of extracting hydrogen from another decalin molecule:



* The symbol "DH" is used here to represent a decalin molecule and "D·" to represent a decalin radical.

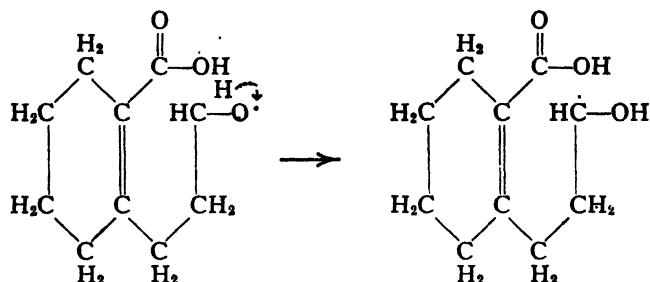
The hydroperoxide formed now decomposes with the loss of a hydroxyl group as before:

VI



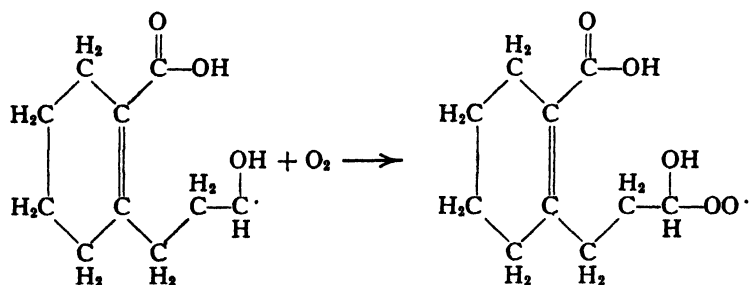
The aldehyde radical formed now rearranges with a 1,2 shift of hydrogen:

VII (a)



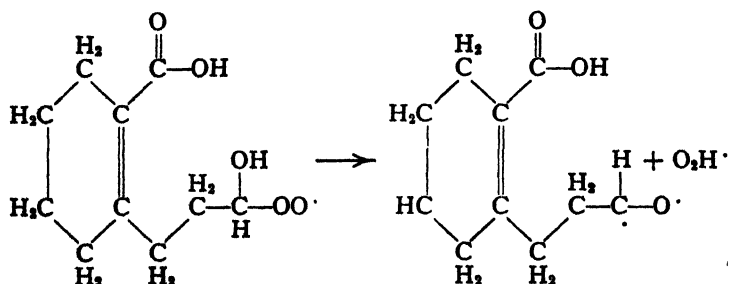
The rearranged radical is now capable of addition of another molecule of oxygen:

(b)

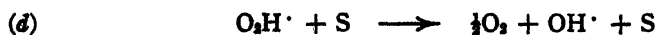


The highly oxygenated tip loses the radical O_2H^\cdot :

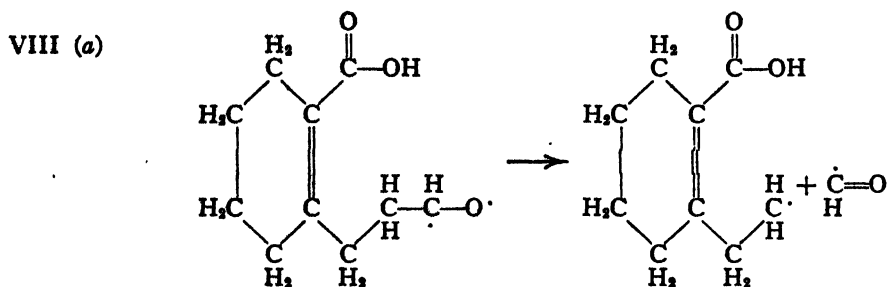
(c)



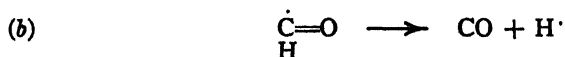
Step VII may be considered to be the abstraction of hydrogen from the radical by a molecule of oxygen. The radical O_2H^\cdot decomposes upon contact with the wall to form neutral oxygen and a hydroxyl group:



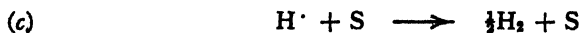
Another 1,2 hydrogen shift to the oxygen is now unlikely. Fission of the C—C bond follows, with the release of the formyl radical:



The formyl radical decomposes to form carbon monoxide and a hydrogen atom:

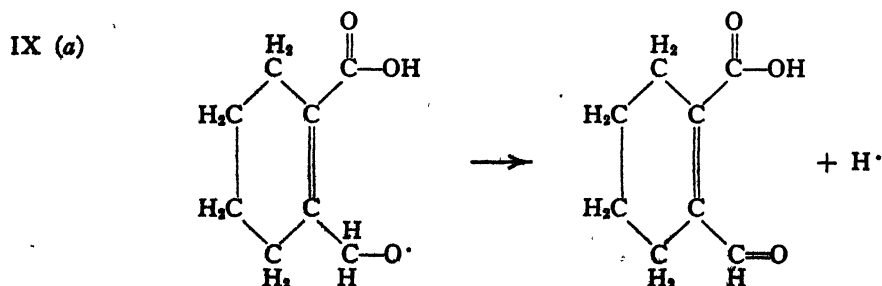


The hydrogen atom is recombined by contact with the surface of the vessel:

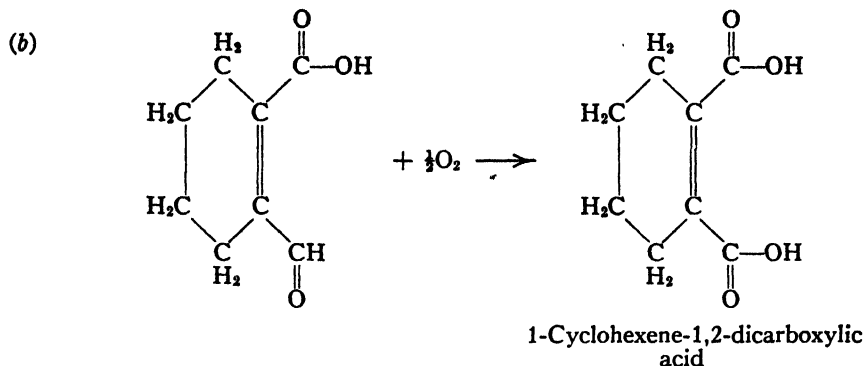


A 9-carbon radical now exists similar to the 10-carbon radical formed by Reaction III and it is capable of going through the same sequence of reactions IV to VIII to form a similar 8-carbon radical.

The results indicate that the destructive oxidation of the molecule stops at this point. It is possible that steps IV, V, and VI occur as before to form the 8-carbon aldehyde radical, but that owing to the influence of the ring or of the double bond, instead of the rearrangement of the aldehyde radical as shown in step VII, the radical stabilizes itself by the formation of the aldehyde group and the loss of a hydrogen atom:



followed by the oxidation of the aldehyde to form 1-cyclohexene-1,2-dicarboxylic acid found among the reaction products:



An independent check on the postulated mechanism for the initiating reaction is possible by comparing the amount of hydrogen formed with the amount that would be expected from the unsaturation in the 1-cyclohexene-1,2-dicarboxylic acid. At 100 hr. approximately 0.006 mole of the acid precipitated from the decalin (per liter) with unsaturation corresponding to 0.012 gm-atoms of hydrogen. At this time 0.064 gm-atoms of hydrogen was collected. However, from the proposed mechanism only two out of the five atoms of hydrogen formed by the complete oxidation of an octahydronaphthalene molecule to form the acid are from the unsaturation in the acid, so that only 0.025 gm-atoms of hydrogen would be expected from unsaturation in the acid.

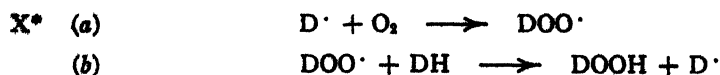
Since only a few milligrams of the acid was formed in each run (about 100 mgm. at 100 hr. in a 100 ml. sample of decalin) a small solubility of the acid in the decalin would make a large percentage error in the quantitative determination of the acid. Allowing for some solubility of the acid in the decalin and for the possibility that the oxidation of the octahydronaphthalene did not always go to completion, thus forming some hydrogen by the initial steps without the formation of a corresponding amount of the final acid, the values for the hydrogen obtained (0.025 gm-atoms at 100 hr.) and the hydrogen expected from an estimate of the unsaturation in the 1-cyclohexene-1,2-dicarboxylic acid (0.012 gm-atoms at 100 hr.) are considered to corroborate the postulated mechanism.

The initiating reaction that has been discussed represents only a small, although important, part of the over-all oxidation reaction. The 1-cyclohexene 1,2-dicarboxylic acid formed at 100 hr. of oxidation only accounts for 1.2% of the total oxygen consumed. However, the complete oxidation of one molecule of the octahydronaphthalene to form the acid results in the formation of nine decalin radicals, each of which is capable of initiating a reaction chain as shown below.

(b) *Accelerated Period of Oxidation*

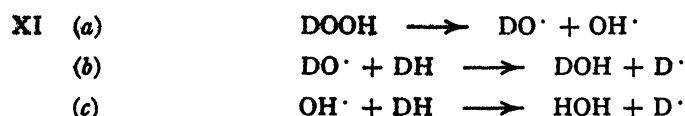
The initiating reaction postulated above provides a source of decalin radicals produced at an estimated rate of 11.4×10^{-4} mole D^{\bullet} per liter of

decalin per hour. It is generally believed (5, 11, 18) that oxygen uptake by hydrocarbons is by a radical-chain mechanism involving the hydroperoxide:



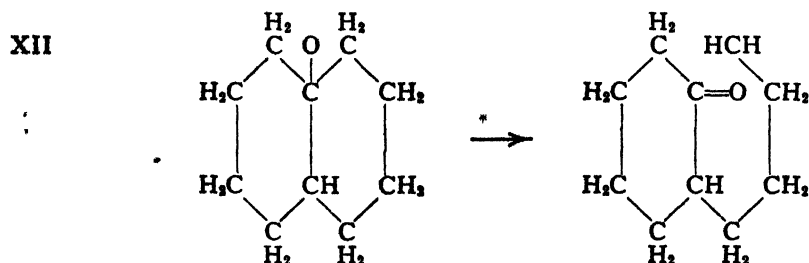
(Some authors (7, 8) however believe that an energy-chain mechanism will account for the facts.)

The hydroperoxide of decalin is known (10) to be a relatively stable compound, so that it would be expected to accumulate in the oxidized decalin. However, the results indicate that not over half of the total oxygen retained by the decalin is in the form of the hydroperoxide. It is postulated therefore that the hydroperoxide decomposes by a series of three reactions that lead to chain branching:



The chain branching resulting from the formation of two decalin radicals for each molecule of the hydroperoxide that decomposes accounts for the autocatalysis observed in the oxygen-retention reaction as shown in Fig. 5. Reaction XI (b) explains the presence of the saturated hydroxy compounds among the oxidation products. Reaction XI (c) explains the acceleration in the rate of water formation observed at 30 to 40 hours. It is assumed that the rate of hydroperoxide decomposition only becomes appreciable at that time. The similarity between the activation energy of the water-forming reaction in the initial and accelerated period is explained, since water is formed by the same reaction in each case.

The acceleration in the rate of formation of volatile carbon can be accounted for by rearrangement of some of the decalinol radicals produced by Reaction XI (a) with ring fission:



and further oxidation of the radical to form more complex compounds including carbon monoxide, acids, aldehydes, etc. Since there is no acceleration in the rate of formation of volatile carbon until 60 hr., Reaction XII cannot occur

*NOTE: The symbol *DH* is used here to represent a decalin molecule, *D*[·] to represent a decalin radical, *DOO*[·] to represent the decalin hydroperoxide radical and *DOOH* to represent decalin hydroperoxide. In later work the symbol *DO*[·] will be used to represent the decalinol radical and *DOH* will represent the decalinol molecule.

to an appreciable extent before this period. The difference between the activation energy observed for the reaction forming carbon monoxide in the initial and in the accelerated periods is explained by the difference in the reaction by which carbon monoxide is formed from the oxidation of octahydronaphthalene and the reaction by which it is formed from the oxidation of the decalinol radical.

Reaction XII explains the presence of carbonyl compounds formed in the accelerated period of the oxidation.

The chain-stopping reaction postulated is the combination of two decalin radicals with an oxygen molecule to form the peroxide:



The reactions X, XI, and XIII postulated to account for the reaction in the accelerated period cannot be a complete description of the accelerated oxidation mechanism, since when considered kinetically they do not explain the independence of the reaction to oxygen concentration nor its observed dependence on decalin concentration to the three-halves power. Moreover a kinetic analysis of these reactions suggests that the rate of oxygen uptake (including the oxygen going to form water) is twice the rate of water formation whereas the observed rate of oxygen uptake (including the oxygen going to form water) from Table I (412.5×10^{-4} mole oxygen per liter per hr.) is four times the rate of water formation (102.4×10^{-4} mole water per liter per hr.).

Part of the difficulty may be due to the assumption of homogeneity of the over-all reaction made in considering it kinetically. It seems quite possible that the oxygen uptake reactions X (a) and XIII are heterogeneous, occurring at the interface between the liquid decalin and the oxygen bubble. The rate of diffusion of the decalin radical to the interface of its orientation in the interface might be the rate-controlling step in the reaction chain X, making the reaction essentially independent of oxygen concentration. The apparent independence of the oxidation reaction to the amount of interface (pumping rate) between the oxygen and the decalin would be explained, qualitatively at least, by the chain-stopping reaction XIII, since chain-stopping as well as oxygen-uptake is dependent on the amount of interface.

Acknowledgments

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MÉTHODE DE SYNTHÈSE DE CÉTONES À PARTIR DES DÉRIVÉS ORGANOMAGNÉSIENS ET DES ORTHOESTERS¹

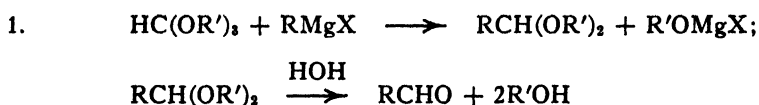
PAR ROGER BARRÉ ET BENOIT LADOUCEUR²

Sommaire

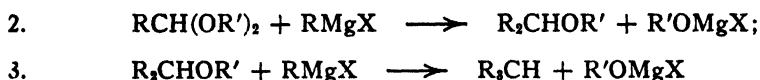
L'action des dérivés organomagnésiens sur les orthoesters fournit une méthode générale de préparation des cétones aliphatiques avec d'assez bons rendements dans plusieurs cas, les meilleurs étant obtenus avec les radicaux en chaîne droite. Avec l'orthocarbonate d'éthyle, on obtient seulement des cétones symétriques; avec les autres orthoesters, on obtient des cétones symétriques ou asymétriques suivant la nature de l'orthoester et du dérivé Grignard. Les rendements maxima (40 à 60%) sont obtenus avec un excès de deux molécules de dérivé organomagnésien par rapport à l'orthoester et un chauffage à reflux de huit heures en milieu étheré.

Introduction

Il se trouve dans la littérature chimique une méthode générale de synthèse des aldéhydes (2, 15, 17, 21) à partir des orthoformiates et des organomagnésiens:

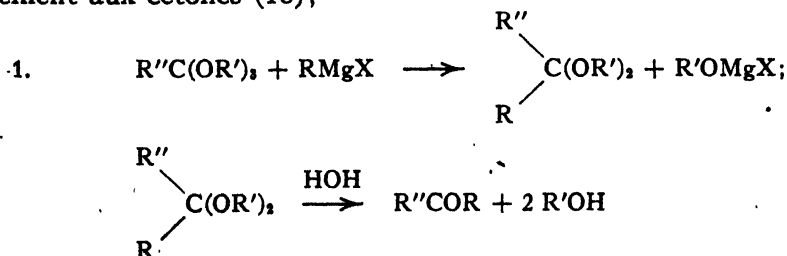


Théoriquement cette réaction peut se poursuivre (19) par réaction subséquente de l'acétal d'après les équations suivantes:



Elle peut conduire alors à des éthers-oxydes d'alcools secondaires et à des carbures.

Dans ces équations, il est possible de voir qu'en remplaçant les orthoformiates par leurs homologues supérieurs, les orthoesters, on peut arriver théoriquement aux cétones (18);

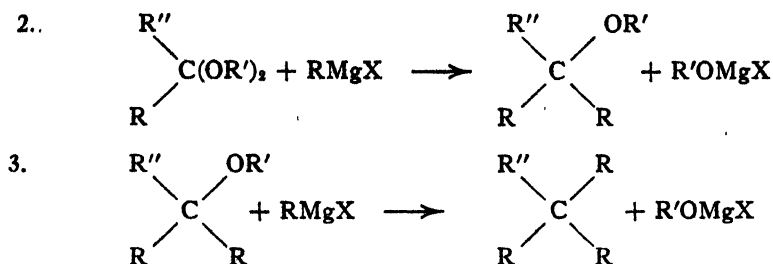


¹ Manuscrit reçu le 5 octobre 1948.

Contribution de l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, Qué.

² Adresse actuelle: Canadian Industries Limited, Beloeil, Que.

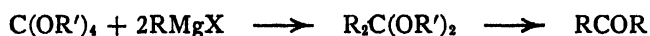
Théoriquement aussi, cette réaction peut se continuer et donner des éthers-oxydes d'alcools tertiaires et des carbures:



Les orthocarbonates peuvent aussi remplacer les orthoformiates et donner les mêmes réactions en passant, en une première phase (8, 18) par les orthoesters:



La réaction subséquente de ces orthoesters se confond avec celle donnée ci-haut. Mais il est à noter cependant que les orthocarbonates conduisent seulement à des cétones et à des carbures symétriques:



Nous avons voulu généraliser la réaction de préparation des aldéhydes par les dérivés Grignard et l'orthoformiate d'éthyle, en l'étendant aux cétones symétriques et asymétriques par l'action de ces mêmes dérivés sur l'orthocarbonate d'éthyle et les autres orthoesters.

Description des expériences

La préparation de cétones par l'action des organomagnésiens sur les orthocarbonates ou les orthoesters n'a pas encore été essayée lorsqu'on examine la littérature chimique. On a seulement préparé des orthoesters par l'action des organomagnésiens sur les orthocarbonates (8, 18). Pour arrêter la réaction à la première phase, on avait plutôt évité le contact prolongé des composés en présence ainsi que le chauffage de mélange après la condensation.

Comme nous voulions obtenir des cétons qui par hydrolyse donneraient des cétones soit avec les orthocarbonates soit avec les autres orthoesters, nous avons laissé la réaction se poursuivre librement puis nous avons cherché ensuite à la favoriser en faisant varier les conditions. Nous voulions cependant éviter les réactions conduisant aux éthers-oxydes et aux carbures.

L'étude de la réaction a été faite en utilisant d'abord l'orthocarbonate et l'orthopropionate d'éthyle, avec le bromure d'éthylmagnésium. Celui-ci a été fait à la façon habituelle dans l'éther éthylique anhydre et utilisé en solution éthérée ou dans d'autres solvants substitués à l'éther; on opère en atmosphère d'azote. Les orthoesters ont été dilués dans leur volume du solvant employé et ajoutés lentement, en proportions variables, au bromure d'éthylmagnésium.

Après la condensation, le mélange a été traité par la chaleur, de différentes façons, puis le complexe organomagnésien formé dans la réaction a été décomposé à froid par l'eau, ensuite par l'acide sulfurique à 25%, qui en même temps hydrolyse le cétal en cétone; dans certains cas une solution aqueuse concentrée de chlorure d'ammonium (qui n'hydrolyse pas le cétal), nous a permis d'isoler ce dernier.

Les produits de la réaction (cétone ou cétal) ont alors été extraits à l'éther; les extraits ont été séchés sur Drierite et fractionnés par distillation. La cétone obtenue a été précipitée à l'état de semicarbazone par le chlorhydrate de semicarbazide. Le cétal, dans les cas où nous l'avons isolé, a dû être hydrolysé afin de libérer la cétone. Les semicarbazones séchées ont permis une identification des cétones synthétisées par leur point de fusion, et une évaluation des rendements obtenus, par leur pesée.

Partie expérimentale

Nous avons d'abord fait réagir les orthoesters et le bromure d'éthylmagnésium dans des proportions équimoléculaires puis nous avons utilisé par la suite un excès d'une à deux molécules de bromure d'éthylmagnésium.

a. Proportions équimoléculaires

Les premiers essais ont été faits dans l'éther anhydre, sans chauffer à reflux après la condensation terminée. Puis pour favoriser la réaction, nous avons chauffé à reflux plus ou moins longtemps (deux à huit heures). Nous avons ensuite élevé la température de réaction en substituant à l'éther après synthèse de l'organomagnésien, des solvants à point d'ébullition plus élevé (benzène, toluène). Enfin dans d'autres essais nous avons enlevé l'éther complètement par distillation (15) ce qui élève encore la température de réaction, soit immédiatement après la condensation ou soit après un chauffage à reflux de huit heures.

Malgré toutes ces variations de condition le rendement maximum en diéthylcétone a atteint 10% seulement de la théorie. Nous avons alors décidé d'utiliser un excès de l'organomagnésien par rapport à l'orthoester.

b. Excès d'une molécule d'organomagnésien

Des essais identiques à ceux décrits ci-haut ont été répétés. L'excès de l'organomagnésien s'est montré favorable à la réaction, car le rendement en diéthylcétone a passé de 10 à 35-40%. L'usage de solvants à haut point d'ébullition (benzène, etc.) au lieu de favoriser la réaction semble l'arrêter quelque peu car le rendement dans ces cas est resté inférieur à 30%. Le temps de chauffage à reflux après la condensation a varié de 4 à 16 h.; le temps optimum est de huit heures.

c. Excès de deux molécules d'organomagnésien

Quelques essais dans l'éther ont suffi à montrer que le rendement en diéthylcétone augmente encore un peu (5 à 10%) quand l'excès de bromure d'éthylmagnésium par rapport à l'orthoester est porté à deux molécules.

Dans ces conditions, i.e., condensation dans l'éther anhydre et chauffage à reflux subséquent de huit heures, plusieurs cétones ont été synthétisées.

Résultats

1. Avec l'orthocarbonate d'éthyle (cétones symétriques)



Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Diéthylcétone*	44	138–139 (10, 9)	137–139
Di- <i>n</i> -propylcétone	57	132–135 (16, 7)	132–132.5
Di- <i>i</i> -propylcétone	12 à 15	136 à 157 (13, 20)	134–136 138–139
Di- <i>n</i> -butylcétone	52	90 (11)	86–89

* Analyse—Calculé: C, 50.32; H, 9.14; N, 29.35%. Trouvé: C, 50.42, 50.62; H, 8.50–8.88; N, 29.31–29.37%.

Les di-*n*-amyl, di-*s*-butyl et di-*t*-butylcétones ont été synthétisées mais les rendements n'ont pu être évalués exactement car elles n'ont pas voulu donner de précipités avec la semicarbazide; les rendements des di-*s*-butyl et di-*t*-butyl cétones ont cependant été faibles car dans les deux cas l'organomagnésien n'a pas beaucoup réagi. Les dibenzyl et diphénylcétones n'ont été obtenues qu'avec un rendement inférieur à 20%.

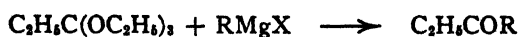
En essayant d'obtenir des composés non symétriques par réaction des orthocarbonates et de deux organomagnésiens différents, nous avons obtenu un mélange de cétones symétriques et non symétriques avec un mauvais rendement.

2. Avec l'orthoacétate d'éthyle (cétones avec un radical méthyl)



Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Méthyléthylcétone	6	135; 143 (11, 12)	142–143
Méthyl- <i>n</i> -propylcétone	17	100; 110 (14, 10)	100–102
Méthyl- <i>n</i> -butylcétone	29	118; 127 (10, 3)	123–125
Méthyl- <i>n</i> -amylcétone	31	122; 127 (4, 10)	121–122

3. Avec l'orthopropionate d'éthyle (cétones avec un radical éthyl)

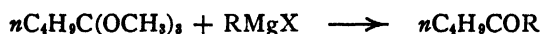


Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
Diéthylcétone	45-52	138-139 (10, 9)	137-138
Ethyl- <i>n</i> -propylcétone	46	110-112 (1, 11)	108-110
Ethyl- <i>i</i> -propylcétone	20	80-95 (10, 6)	90-91
Ethyl- <i>n</i> -butylcétone	55	99-100 (11)	98-99
Ethyl- <i>i</i> -butylcétone	32	143 (5)	139-140 140-142
Ethyl- <i>n</i> -amylcétone	42	112-117 (11, 3)	110-111
Ethyl- <i>i</i> -amylcétone	40	132-133 (3)	119-120*
Ethyl- <i>n</i> -hexylcétone	43**	111-112 (11)	110-111
Ethyl- <i>n</i> -décylcétone	40	90- (11)	80-95

* Point de fusion bas même après plusieurs cristallisations; la substance obtenue est probablement un mélange d'isomères. Calculé: C, 58.39; H, 10.33; N, 22.68%. Trouvé: C, 58.53-58.57; H, 10.27-10.47; N, 21.94-22.01%.

** Rendement calculé d'après le poids de semicarbazone non purifiée.

L'éthyl-benzylcétone a été synthétisée avec 13% de rendement. L'éthyl-*s*-butylcétone a aussi été synthétisée mais avec un rendement inférieur.

4. Avec l'ortho-*n*-valérate de méthyle (cétones avec un radical butyl)

Cétones	Rendements, %	Semicarbazones	
		P.f. rapporté, °C.	P.f. obtenu, °C.
<i>n</i> -Butyléthylcétone	60	99-100 (11)	101-102
<i>n</i> -Butyl- <i>n</i> -amylcétone	39*	—	78-79

* Rendement calculé d'après le poids de semicarbazone non purifiée. Le point de fusion de cette semicarbazone n'est pas rapporté dans la littérature. Calculé: C, 61.93; H, 10.86; N, 19.70%. Trouvé: C, 61.79-61.86; H, 10.88-11.06; N, 19.66-19.69%.

Tous les dérivés halogénés utilisés dans les synthèses des organomagnésiens ont été des bromures sauf le dérivé benzyle qui a été employé sous forme de chlorure.

Dans la méthode de préparation des cétones décrites précédemment, l'addition d'un excès de dérivé organomagnésien par rapport à l'orthoester devrait en principe nous donner plus de réactions secondaires et par conséquent diminuer le rendement en produits cétoniques. Mais la bibliographie nous montre qu'il faut élever considérablement la température du reflux pour

effectuer le passage aux éthers oxydes secondaires et aux hydrocarbures prévus par la théorie. Nous l'avons d'ailleurs constaté dans la partie expérimentale; en effet, l'élévation de température de la réaction en changeant le solvant (benzène ou toluène à la place de l'éther) diminue les rendements. Au contraire, en faisant refluer à la température de l'ébullition de l'éther (36° C.), on peut limiter la réaction à la phase céta; cependant à cette température la réaction est lente et les produits formés très insolubles. C'est seulement par l'addition d'un excès de dérivé organomagnésien qu'on peut obtenir un rendement appréciable.

Remerciement

Nous tenons à remercier Canadian Industries Limited qui, par l'octroi à l'Université de Montréal d'une bourse de recherches dont Benoît Ladouceur fut le détenteur 1944 à 1947, a permis la poursuite de ce travail, partie des conditions requises pour l'obtention du grade de Ph. D.

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ORGANIC REAGENTS FOR PLATINUM METALS

I. THE DETERMINATION OF PALLADIUM WITH 1,10-PHENANTHROLINE¹

By D. E. RYAN² AND P. FAINER

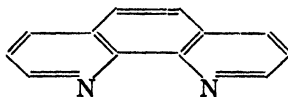
Abstract

Palladium may be precipitated quantitatively with 1,10-phenanthroline from palladous chloride solutions; variations in the hydrochloric acid concentration from 1 to 20% had no effect on the precipitation. The reagent yields no precipitates with other platinum metals under similar conditions; slightly high results, however, were obtained when palladium was precipitated from solutions containing these metals. The precipitate has the composition $C_{12}H_8N_2PdCl_2$ and may be used as a weighing form for palladium. A micro-volumetric method for palladium using 1,10-phenanthroline is described. Small amounts of platinum (as Pt^{+4}) do not interfere.

Introduction

The reactions of the platinum metals with various organic compounds have been studied extensively. Some of these reactions have formed the basis for analytical procedures for the platinum metals; many of the researches, however, have been concerned with the study of the methods of preparation and stereoisomerism of the various compounds produced. The present investigation was carried out with a view to extending the use of organic reagents for platinum metal determinations—and to relating the configuration of the organic compounds with their ability to react with these metals.

In a large series of preliminary experiments, 5-ml. aliquots of the standard platinum metal solution under investigation were diluted and acidified to six different acid conditions (0.05 and 0.30 *N* in hydrochloric acid, nitric acid, and aqua regia). The organic reagent was added and the solution gently boiled for two hours. If a precipitate formed, the mixture was filtered and the filtrate tested for the metal. As a result of this investigation, it was found that 1,10-phenanthroline



would precipitate palladium quantitatively from a hydrochloric acid solution of palladous chloride. No precipitates were obtained with solutions of Ru^{+3} , $Ir^{+4,+3}$, Rh^{+3} , Pt^{+4} under similar conditions.

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Contribution from the Department of Chemistry, University of New Brunswick, Fredericton, N.B., with financial assistance from the National Research Council of Canada.

² Present address: Illinois Institute of Technology, Chicago 16, Illinois, U.S.A.

Gravimetric Determination of Palladium

Materials

1. Palladous chloride—solutions of palladous chloride standardized by dimethylglyoxime method (3).

Solution 1—6.96 mgm. palladium per 10 ml.

Solution 2—8.45 mgm. “ “ “ “

2. 1,10-Phenanthroline—0.5% aqueous solution.

Methods

To 10-ml. aliquots of the standard palladous chloride solution were added varying amounts of concentrated hydrochloric acid. Six milliliters of the 1,10-phenanthroline reagent was then added and the volume of the solution made up to 50 ml. These solutions were allowed to stand for one hour, and the precipitates were filtered through Whatman No. 42 filter papers, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as the metal. The results are shown in Table I.

TABLE I

PRECIPITATION OF PALLADIUM WITH 1,10-PHENANTHROLINE AND SUBSEQUENT WEIGHING AS THE METAL

Palladium taken, mgm.	Palladium recovered, mgm.	Palladium taken, mgm.	Palladium recovered, mgm.
6.96	6.95	6.96	6.96
6.96	6.98	6.96	6.97
6.96	6.96	6.96	6.95
6.96	6.95	6.96	6.95
6.96	6.95	6.96*	6.88*
6.96	6.97	6.96**	6.90**
6.96	6.97		

* Average of several results in which no hydrochloric acid was added.

** Average of several results in which <4 ml. 1,10-phenanthroline was added.

In all other cases the hydrochloric acid concentration was varied from 1 to 20%.

Table I shows that palladium may be quantitatively precipitated with 1,10-phenanthroline from solutions varying from 1 to 20% in hydrochloric acid. Although 1,10-phenanthroline does not precipitate nickel or the platinum metals previously mentioned, under these conditions, it was found that results were 0.2 to 0.4 mgm. high in the presence of equivalent amounts of these metals.

In the absence of chloride ion, precipitates similar to the above were obtained in the presence of fluoride, bromide, or iodide. Palladous nitrate in dilute nitric acid also gave a precipitate with the reagent. This precipitate proved fairly soluble in water.

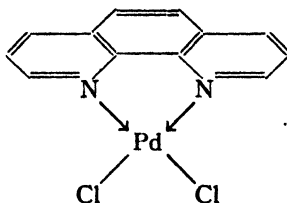
Composition of the Complex

Oven-dried (110° C.) samples of the complex were analyzed for palladium, for nitrogen (4), and for chlorine (1, 2). The results obtained, as shown in Table II, suggest that the complex consists of 1,10-phenanthroline, palladium, and chlorine in the ratio 1:1:2 respectively; this indicated a molecular formula $C_{12}H_8N_2PdCl_2$. The theoretical percentages for such a compound are also shown in Table II. The precipitate obtained from palladous nitrate and 1,10-phenanthroline suggested, on analysis, a similar structure, $C_{12}H_8N_2Pd(NO_3)_2$.

TABLE II
COMPOSITION OF COMPLEX

Composition	Per cent found	Number of determinations	Theoretical per cent for $C_{12}H_8N_2PdCl_2$
Palladium	29.2	8	29.8
Nitrogen	7.86	6	7.83
Chlorine	20.0	3	19.8

The dichloride proved extremely insoluble, even in nonpolar solvents. Dissolution in concentrated sulphuric acid and subsequent test with silver nitrate yielded a positive result for chloride ion. Aqueous solutions of the dinitrate complex yielded positive brown ring and diphenylamine tests for nitrate ion on standing. One would expect few ions to be present if no hydrolysis occurs in solution. Conductance measurements should help clear up this point, and further work is to be done in this direction. On the basis of analysis it seems probable that the structural formula of the complex is as follows:



Results obtained by filtering the precipitate through a fine sintered glass crucible, drying at 110° C., and weighing as $C_{12}H_8N_2PdCl_2$ are shown in Table III. These results indicate that palladium may be determined in this manner.

TABLE III
PRECIPITATION OF PALLADIUM WITH 1,10-PHENANTHROLINE AND SUBSEQUENT WEIGHING AS $C_{12}H_8N_2PdCl_2$

Palladium taken, mgm.	Palladium recovered, mgm.	Palladium taken, mgm.	Palladium recovered, mgm.
16.90	16.79	16.90	16.78
16.90	16.78	16.90	16.77

The Microvolumetric Determination of Palladium

Material and Equipment

1. Ferrous sulphate—analar grade,
2. Palladous chloride—standard solution containing 0.845 mgm. palladium per ml. and approximately 0.5% with respect to hydrochloric acid,
3. 1,10-phenanthroline—standard solution containing 1.00 mgm. of the monohydrate per ml.,
4. Hydrochloric acid—approximately 1:1 solution,
5. Fisher electrophotometer, AC model.

Development of Method

Since ferrous iron combines with 1,10-phenanthroline to form a soluble red ferrous phenanthroline complex, it was thought that palladium might be determined volumetrically by adding excess phenanthroline and determining this excess by measuring the color produced on addition of ferrous iron. Owing to the necessary acidity of the precipitating medium, it was found that a canary yellow color, instead of the familiar red ferrous phenanthroline color, was developed on addition of ferrous iron to the filtrate. The hue of the solution changed slowly with time and finally assumed the familiar reddish brown color. Any difficulty involved here was overcome by using a definite time interval before taking electrophotometer readings—both in the construction of a standard curve and in the actual analyses.

Preparation of Reference (or Standard) Curve

In constructing a reference curve, the following procedure was carried out. To x ml. of standard 1,10-phenanthroline were added a few drops of 1:1 hydrochloric acid and enough distilled water to make the final volume 100 ml. Approximately 0.1 gm. of analar grade ferrous sulphate (an excess) was added and the electrophotometer scale reading, using 425B filter, taken 15 min. after mixing.

Procedure

Samples of the standard palladous chloride solution were measured by means of a microburette into 250-ml. wide-mouthed Erlenmeyer flasks and the volume made up to approximately 25 to 30 ml. The standard 1,10-phenanthroline solution was added from a microburette, dropwise, until an excess of 2 to 4 ml. was present. After allowing to stand for one hour, the precipitate was filtered through a sintered glass crucible and washed well with distilled water. The volume of the filtrate was made up to 100 ml. in a volumetric flask, an excess of ferrous sulphate then added, and the color produced with the excess phenanthroline measured 15 min. after mixing. From the observed scale reading, the number of milliliters of standard phenanthroline added in excess can be determined by reference to the standard curve. Results are shown in Table IV.

The table shows that palladium may be determined quantitatively, even in the presence of small amounts of platinum or rhodium, by this method. Ions which also form complexes with 1,10-phenanthroline (as Cd^{++} , Cu^{++} , Zn^{++} , Co^{++} , Ni^{++} , Cr^{++} , Ru^{++} , etc.) must, of course, be absent. Further work regarding interferences is to be carried out.

TABLE IV
THE MICROVOLUMETRIC DETERMINATION OF PALLADIUM WITH
1,10-PHENANTHROLINE

Palladium taken, mgm.	Platinum metal added,* mgm.	Palladium found, mgm.
8.45	—	8.42
8.45	—	8.51
8.45	—	8.40
6.70	—	6.67
4.43	—	4.49
4.23	—	4.23
3.86	—	3.89
1.99	—	2.03
1.69	—	1.70
1.69	—	1.67
0.84	—	0.86
0.55	—	0.53
4.23	0.75 Pt	4.23
4.23	1.50 Pt	4.25
4.23	2.25 Pt	4.24
4.23	1.00 Rh	4.20
4.23	1.00 Rh	4.19

* Platinum added as H_2PtCl_6

Rhodium added as RhCl_3 .

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ORGANIC REAGENTS FOR PLATINUM METALS

II. THE GRAVIMETRIC DETERMINATION OF RHODIUM¹

BY R. L. HAINES AND D. E. RYAN²

Abstract

Rhodium may be precipitated quantitatively with 2-mercaptobenzoxazole or 2-mercaptobenzothiazole. An acetic acid precipitating medium is preferred; slight variations in the concentration of acid, when nitric acid was used, caused low results. Several similar type organic compounds showed no advantages over the above two. The complex appears to have three molecular weights of the reagent combined with one atomic weight of rhodium.

Introduction

The reactions of organic sulphide compounds with many metals have been studied extensively. Currah and coworkers (1) investigated several organic sulphides as reagents for the platinum metals and reported the first organic precipitant, thiobarbituric acid, for rhodium. Among the large number of organic compounds undergoing preliminary investigation, in the authors' laboratories, were five mercapto compounds. The efficiency of these compounds for the precipitation of the platinum metals is being examined.

In all preliminary investigations, tests were carried out under varying acid concentrations (0.05 and 0.3 *N* in hydrochloric acid, nitric acid, and aqua regia). If, after boiling gently for two hours, a precipitate formed, the mixture was filtered and the filtrate spot tested (after destruction of organic matter) for the metal. The stannous chloride spot test was used for rhodium (3). Complete precipitation for rhodium with 2-mercaptobenzothiazole was found in 0.05 *N* nitric acid solution while other reagents—as 2-mercaptobenzoxazole and 2-mercapto-4-phenylthiazole—gave slightly low results. The following is a report of the successful application of 2-mercaptobenzothiazole and 2-mercaptobenzoxazole to the determination of rhodium.

Reagents

1. Rhodium trichloride—solution standardized with hydrogen sulphide (2).
2. 2-Mercaptobenzoxazole—solution containing 1.5 gm. in 100 ml. glacial acetic acid,
3. 2-Mercaptobenzothiazole—solution containing 1.5 gm. in 100 ml. glacial acetic acid,
4. Ammonium chloride—approximately 1% aqueous solution.

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² Present address: Illinois Institute of Technology, Chicago 16, Illinois, U.S.A.

Determination of Rhodium with 2-Mercaptobenzoxazole*Method*

To an aliquot of the standard rhodium solution in a 150 ml. beaker, 5 ml. of the ammonium chloride solution was added and the volume made up to approximately 50 ml. The solution was then heated to the boiling temperature and 3 to 4 ml. of the reagent added. After digestion for one hour at this temperature, the mixture, upon cooling, was filtered through Whatman No. 42 filter paper. The precipitate was washed with dilute acetic acid, ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as rhodium metal. Results are shown in Table I. The effect of different periods of digestion is also shown in Table I.

TABLE I
DETERMINATION OF RHODIUM WITH 2-MERCAPTOBENZOXAZOLE

Rhodium taken, mgm.	Rhodium recovered, mgm.	Digestion period, min.
11.35	10.08	10
11.35	10.37	10
11.35	11.02	20
11.35	10.81	20
11.35	11.12	45
11.35	11.25	45
11.35	11.34	60
11.35	11.41	60
11.35	11.37	60
11.35	11.34	60
11.35	11.30	60
11.35	11.33	60
11.35	11.40	60
11.35	11.36	60

Table I shows that rhodium may be determined quantitatively by this method but that a digestion period of at least one hour is necessary.

Composition of Complex

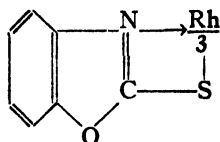
A rhodium precipitation was carried out with 2-mercaptobenzoxazole reagent. The precipitate was filtered, washed with dilute acid and water, dried under reduced pressure, and weighed. The residue was then ignited in air, reduced in hydrogen, cooled in carbon dioxide, and weighed as rhodium metal. Results are shown in Table II.

If three molecular weights of 2-mercaptobenzoxazole were combined with one atomic weight of rhodium, the latter replacing one hydrogen of each 2-mercaptobenzoxazole molecule, the amount of rhodium present would be 18.6%. Comparison of the complexes of metals with similar organic

TABLE II
COMPOSITION OF COMPLEX

Weight of complex, mgm.	Weight of rhodium, mgm.	Per cent rhodium
89.40	15.70	17.6
85.75	15.16	17.7
87.45	15.44	17.7
90.86	15.95	17.6
91.70	16.18	17.6

compounds leads to the conclusion that the above complex probably has the following structure:



Determination of Rhodium with 2-Mercaptobenzothiazole

Methods

The first experiments with this reagent were carried out using an alcoholic solution of the reagent and precipitating from a nitric acid (0.05 *N*) solution. Since slight variations in the concentration of this acid produced low results,

TABLE III

Determination No.	Rhodium taken, mgm.	Rhodium recovered, mgm.
1	7.34	7.40
2	7.34	7.33
3	7.34	7.37
4	7.34	7.36
5	7.34	7.32
6	7.34	7.38
7	7.34	7.37
8	7.77	7.77
9	7.77	7.80
10	7.77	7.70
11	7.77	7.80
12	7.77	7.73
13	13.97	13.96
14	13.97	13.97
15	13.97	13.93
16	13.97	13.91
17	13.97	14.03
18	13.97	13.91
19	11.35	11.35
20	11.35	11.33
21	11.35	11.39

Nos. 1-12: Alcoholic reagent solution and rhodium precipitated from 0.05 *N* nitric acid solution.

Nos. 13-18: Alcoholic reagent solution and rhodium precipitated from solution approximately 1 *N* in acetic acid.

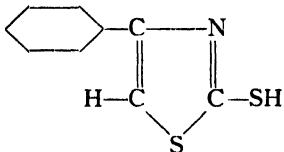
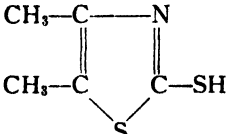
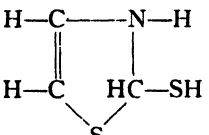
Nos. 19-21: Reagent dissolved in glacial acetic acid.

the method finally adopted was as with the benzoxazole. Results are shown in Table III.

It should be noted that the amount of reagent dissolved in acetic acid can be easily regulated. More or less reagent than the 1.5 gm. in 100 ml. of acid could be used, the actual quantity depending on the amount of rhodium to be precipitated. Slight variations in the acetic acid concentration had little effect on the degree of precipitation. The addition of ammonium chloride aided in the coagulation of the precipitate and made the precipitate more easily handled.

Three other compounds—with similar reactive groupings—were investigated to some extent. All these investigations were carried out in acetic acid media with the filtrates spot tested for rhodium. Results are shown in Table IV.

TABLE IV
SPOT TESTS WITH SIMILAR REAGENTS

Reagent	Formula	Acid strength			
		0.1 N	0.5 N	1.0 N	3.0 N
2-Mercapto-4-phenylthiazole		P	P	C	P
2-Mercapto-4,5-dimethylthiazole		P	P	P	N
2-Mercaptothiazoline		S	S	S	P

N No precipitation
S Very slight precipitation
P Partial precipitation
C Complete precipitation

These compounds show no advantages over the above reagents as precipitants for rhodium. In 3.0 *N* acetic acid medium, a strong red color was developed with 2-mercapto-4,5-dimethylthiazole; this might show promise as a colorimetric reagent for rhodium.

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THE DETERMINATION OF NITRATES IN COLORED SOIL EXTRACTS¹

F. J. SOWDEN AND H. J. ATKINSON

Abstract

In highly colored soil extracts, it was found impossible to determine nitrates directly by the phenoldisulphonic acid color reaction. Attempts to remove the coloring matter by oxidation or absorption were not successful. The most satisfactory method was found to be reduction of the nitrate to ammonia with Devarda's alloy in 0.1 *N* sodium hydroxide solution in the cold after the removal by steam distillation, of any ammonia that might be present in the extract. The ammonia formed from the nitrate was steam distilled into 0.01 *N* hydrochloric acid solution and determined colorimetrically by Nessler's reagent using a Klett-Summerson photoelectric colorimeter. The recovery of nitrates from the colored solutions and from standards was satisfactory. The aliquot taken for the determination should contain not more than 0.125 mgm. nitrogen as nitrate.

Introduction

The determination of the nitrate content of soils is usually made on an aliquot of a water extract by means of the phenoldisulphonic acid method (2). In order to obtain a clear solution, a small amount of the salt of a heavy metal, e.g., copper sulphate or aluminum sulphate (3), is added to the extractant as a flocculating agent and the extract is subsequently treated with calcium hydroxide to precipitate the hydroxides of the metals. This procedure is effective with the majority of soils.

Recently, during a nitrification study in which an ammonia-treated waste sulphite liquor product had been added to a soil (9), it was found impossible to obtain a clear extract in the above manner. The ligninsulphonic acids were water soluble and were not removed in the clarification process. For the nitrate color reactions, organic matter must be completely removed, as traces of organic materials give a considerable amount of color when the dried or concentrated extract is treated with phenoldisulphonic acid.

An attempt was made to remove the coloring material by absorption but neither the basic nor acidic amberlite resins, nor superfiltrol, would remove all the color. Charcoal from various sources would decolorize the solution but it also removed a large percentage of nitrogen from a standard solution of potassium nitrate, and the absorbed anion could not be freed from the charcoal by washing.

Oxidizing agents such as bromine and permanganate have been used to remove organic matter from soil extracts, but, in the present work, neither would sufficiently remove the ligninsulphonic acids to give a clear solution when the evaporated material was treated with phenoldisulphonic acid. Plice (6) suggested the use of superoxol and it was found that this would remove the

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organic matter, but the method was time-consuming, as repeated treatments were necessary. Moreover the results were very high owing to the presence of some nitrate nitrogen in the superoxol and to the oxidation of the ammonia in the waste sulphite liquor material to the nitrate form. The method might possibly be satisfactory where the soil extract contains large amounts of nitrates, very little ammonia, and organic material that is easily oxidized, but it was not satisfactory in this case.

Berge (1) has suggested that it is not necessary to remove the interfering color if a photoelectric colorimeter is available, as two aliquots can be evaporated to dryness and treated with the phenoldisulphonic acid. The color is developed in one of these and the other is used as a "blank" reading. Experiment showed, however, that the blank reading was very variable for identical aliquots. Thus, with low amounts of nitrate, the error might be very large and it was concluded that the method could not be used.

Experimental

In view of the failure of the above methods to remove the interfering color, it seemed that the alternative was to reduce the nitrate to ammonia, distill the ammonia from the colored solution, and determine it with Nessler's reagent. Olsen (4, 10) used Devarda's alloy (copper, aluminum, and zinc fused in a 50 : 45 : 5 ratio) to determine nitrate in soil, but his method required large quantities of nitrate. Pynne (7) has described methods for determining nitrate in plant materials using Devarda's alloy or titanous hydroxide for its reduction. With plant materials, any ammonia in the original material was distilled from calcium hydroxide and special precautions were taken to eliminate the possibility of any nitrogenous material being broken down to liberate ammonia. In the soil extracts in question, this interference was less likely to be serious but needed to be guarded against since some of the ammonia from the lignosulphonate was liberated by alkali and more by alkaline permanganate. Therefore, one of the methods suggested by Pynne was followed in principle although it was found necessary to make considerable changes in the details of the procedure to render it suitable for determining the small amounts of nitrate present in the soil extracts. The details of the method as finally adopted are as follows.

An aliquot (usually 20 ml.) was transferred to a 100 ml. Kjeldahl flask, made 0.1 *N* with sodium hydroxide, and steam distilled until there was no test for ammonia with Nessler's reagent, or until the distillate failed to change the color of two or three drops of methyl red in 10 or 15 ml. of water made acid with one drop of 0.01 *N* hydrochloric acid. Either test will detect traces of ammonia. The distillation was carried out in the apparatus described by Redemann (8). The ammonia was completely removed in three to five minutes, after which the flask was cooled. A small amount (approximately 0.5 ml.) of normal sodium hydroxide solution was added to compensate for the water that condensed during steam distillation, and 0.200 gm. of 100 mesh Devarda's alloy were introduced. The flask was stoppered with a rubber

stopper through which passed a glass tube containing glass wool wetted with 0.1 *N* hydrochloric acid to absorb any ammonia that might be carried away by the hydrogen evolved in the reaction. It was shaken several times at intervals of approximately 10 min., then left overnight. In the morning the acid was washed into the flask and the ammonia distilled into 5 ml. of 0.01 *N* hydrochloric acid until a volume of 35 to 40 ml. was obtained. It was found advisable to cut off the flow of steam to guard against any loss of ammonia while the Kjeldahl flask was being connected. The distillate was transferred to a 50 ml. volumetric flask, treated with 1 ml. of Nessler's reagent (prepared as described by Peters and Van Slyke (5)) and made to the mark. The optical density of the solution was then read in a Klett-Summerson photo-electric colorimeter using a blue filter. The concentration of ammonia in solution was obtained from a curve prepared by using a standard 0.001 *N* solution of ammonium sulphate, aliquots up to 25 ml. being treated with Nessler's reagent. A significant reading was obtained when the reagents only were used and this had to be deducted.

To test the accuracy of the method, a series of aliquots of a standard nitrate solution containing 0.01 mgm. nitrogen per ml. were analyzed. The recovery

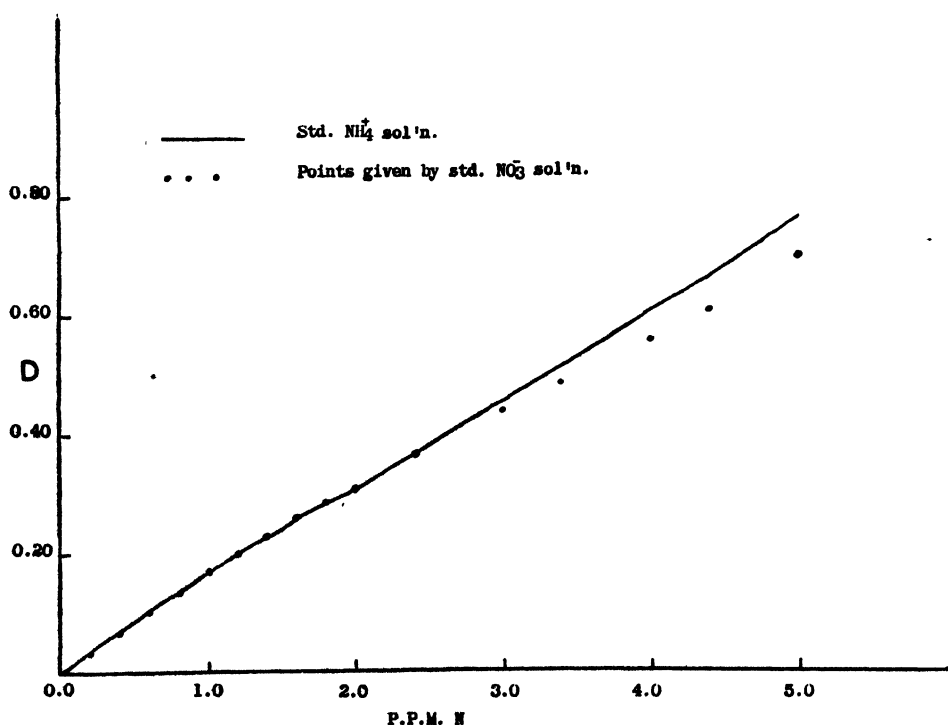


FIG. 1. Curve for standard solution.

is shown graphically in Fig. 1 where optical density is plotted against parts per million nitrogen. The solid line is the curve given by the standard ammonia solution calculated to parts per million nitrogen, and the circles show the density of color developed by the ammonia formed by reduction of

the nitrate. Most of the points on the curve represent averages of several determinations. The agreement was good up to 2.5 p.p.m. (0.125 mgm. nitrogen as nitrate). In this range the recovery was very close to the theoretical. The low recovery at higher concentrations appeared to be the result of incomplete distillation of the ammonia since, when the aliquot was doubled and 70 to 80 ml. was distilled and made up to 100 ml., the color formed was almost identical with that given when the procedure described in the method was followed. In general, it was found more satisfactory to use the smaller aliquot and keep the concentration below 2.5 p.p.m. nitrogen.

The nitrate curve in these higher concentrations seemed to be reproducible, however. In an experiment where known amounts of nitrate were added to soil extracts, good recovery was obtained as shown in Table I. As was to be

TABLE I
RECOVERY OF NITRATE ADDED TO SOIL EXTRACTS

Sample	p.p.m. N in soil extract	p.p.m. N added	Total p.p.m. N present	P.p.m. N recovered	
				NH ₄ curve	NO ₃ curve
A	2.60	2.00	4.60	4.15	4.57
B	2.40	2.00	4.40	4.05	4.47
C	1.65	2.00	3.65	3.45	3.70

expected, the recovery was low when the standard ammonia curve was used. If, however, the concentration was read from the nitrate curve to allow for the incomplete distillation of ammonia, the amount of nitrogen found was equal to the theoretical. Since this was an empirical correction, it seemed likely that good agreement was secured only because the distillation conditions were carefully standardized.

When small amounts of nitrate were added to two solutions of the waste sulphite liquor material from which the ammonia had been removed by distillation with alkali, results as shown in Table II were obtained. These would indicate that there was no breakdown of the organic material to yield ammonia on treatment with Devarda's alloy.

TABLE II
RECOVERY OF NITRATE ADDED TO SOLUTIONS OF WASTE SULPHITE LIQUOR SOLIDS

p.p.m. N added	P.p.m. N recovered	
	Solution A	Solution B
0.20	0.17	0.17
0.40	0.36	0.38
0.80	0.78	0.76

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THE PREPARATION OF CYANAMIDE, UREA, AND RELATED COMPOUNDS LABELED WITH LONG-LIVED RADIO-ACTIVE CARBON¹

BY S. H. ZBARSKY² AND ISABEL FISCHER

Abstract

The following compounds have been prepared labeled with C¹⁴: cyanamide, urea, thiourea, dicyandiamide, and guanidine nitrate. Cyanamide was synthesized by heating radioactive barium carbonate at 850°C. in a stream of ammonia and extracting with water the barium cyanamide so formed. Urea and thiourea were prepared from cyanamide by hydrolysis under suitable conditions. When an aqueous solution of cyanamide was heated, its dimer, dicyandiamide, was obtained and the latter compound was converted to guanidine nitrate by fusing with ammonium nitrate at 175° to 185° C. The preparations of the above materials were carried out on a 5 to 10 millimole scale, and good yields were obtained in each case.

Introduction

At the present time the long-lived radioactive isotope of carbon, C¹⁴, is supplied to investigators chiefly in the form of barium carbonate although other forms are becoming available.* Because of the limited value of barium carbonate or carbon dioxide in organic syntheses, it is often necessary to convert them to simple organic intermediates that can then be used in further syntheses. The present investigation into the synthesis of labeled cyanamide was undertaken because cyanamide appeared to be a most suitable intermediate in the synthesis of a number of compounds of biological interest, e.g., urea, guanidine, arginine, purines, and pyrimidines (1, 2, 3, 4, 5, 8). Furthermore, the methods described in the literature for the synthesis of cyanamide and its conversion to compounds related to urea were simple and could be applied in laboratories with limited facilities. Franklin (4) reported that when ammonia is passed over heated alkali carbonates, the latter are converted to the corresponding cyanamide salts from which cyanamide can be easily obtained (1, 2). In the present work this method has been developed for the synthesis of radioactive cyanamide from radioactive barium carbonate in 10 millimole quantities in yields of the order of 70%. Urea was prepared from labeled cyanamide by hydrolysis in an acid medium. By combining these two procedures so as to eliminate the necessity of first isolating cyanamide, a more direct and less time-consuming method was developed for the preparation of labeled urea. Thiourea was obtained by passing hydrogen sulphide through a heated acid solution of cyanamide in the presence of antimony pentasulphide (6). By heating a faintly ammoniacal solution of cyan-

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* Catalog A, Tracerlab Inc., Boston, Mass.

amide, dicyandiamide was prepared (1, 2), and the latter compound, when fused with ammonium nitrate, yielded guanidine nitrate (3).

In order to measure the radioactivity present in the synthesized compounds they were first oxidized and the carbon dioxide formed was precipitated as barium carbonate. The β -activity present in the barium carbonate samples was then measured using an end-window type of Geiger-Müller counter tube. It was found that the activities of the synthesized compounds agreed with that of the barium carbonate used as original starting material within the limits determined by the counting error. This finding indicated that in the preparations to be described there was no measurable loss of C^{14} due to exchange with carbon dioxide from the air and that the rates of reaction of the C^{12} and C^{14} compounds were not appreciably different.

Methods

In order to oxidize the carbon of the prepared compounds to carbon dioxide and to collect the gas, the method described by Van Slyke and Folch (7) was used. Weighed samples of the materials were oxidized by heating with a mixture of fuming sulphuric, phosphoric, chromic, and iodic acids, and the carbon dioxide produced was collected and measured quantitatively in a Van Slyke-Neill manometric apparatus. After the manometric readings had been taken to permit a quantitative determination of the carbon content of the sample oxidized, the carbon dioxide was expelled from the extraction chamber of the manometric apparatus and absorbed in 7 ml. of 4 *N* sodium hydroxide solution contained in a 15 ml. centrifuge tube. Preliminary experiments showed that by this procedure all except 0.2% of the C^{14} introduced into the extraction chamber as carbon dioxide could be forced out into the sodium hydroxide solution. Presumably the small residual activity was present in carbon dioxide adsorbed on the glass wall of the extraction chamber since it was possible to flush out the C^{14} with nonradioactive carbon dioxide.

The carbonate formed in the sodium hydroxide solution was precipitated by the dropwise addition of a saturated solution of barium chloride. The suspension of barium carbonate was centrifuged and the supernatant fluid was discarded. It was found that with the amounts of radioactive carbon used in the present work no measurable activity remained in the supernatant liquid. The precipitate was washed five times with small volumes of water. This washing was necessary in order to ensure the removal of excess alkali since it was found that the presence of alkali caused the formation of irregular layers of barium carbonate in the following stage of the procedure.

The barium carbonate in the centrifuge tube was suspended in a small volume of water (0.5 ml.) and the suspension was pipetted on to a weighed aluminum disk that had been cleaned and slightly etched by immersion in 5 *N* sodium hydroxide solution for one minute. The aluminum disk was 1½ in. in diameter and 0.014 in. thick, with a flat, circular depression 1 in. in diameter and ¼ in. deep. The barium carbonate suspension was pipetted on to the disk so that it was confined to the circular depression. The disk was heated

under infra-red lamps the height of which was adjusted to permit slow drying of the precipitate. It was found that if drying occurs too rapidly, irregular layers form. When the suspension had dried to a sludge the disk was agitated slightly to spread the barium carbonate in a uniform layer. If the precipitate tended to accumulate along part of the circumference of the circular depression it could be made to move toward the center by tapping gently the opposite edge of the disk. The suspension was finally heated to complete dryness and a layer of barium carbonate was formed that was of uniform thickness and adhered strongly to the aluminum. The disk was then weighed again in order to obtain the weight of the layer of barium carbonate.

A study was also made of the use of organic solvents such as acetone and ethanol as agents in which to suspend the barium carbonate. It was found that acetone caused the barium carbonate to become granular and it then became difficult to prepare layers of uniform thickness. When ethanol was used extreme care was necessary to prevent the suspension from running over the edge of the disk. On the other hand, the surface tension of water is sufficiently great to keep the suspension within the circular depression of the disk. Furthermore, layers prepared from ethanol suspensions did not adhere to the aluminum as strongly as did those prepared from water suspensions.

The β -activity in the barium carbonate on the disk was measured using an end-window type, self-quenching Geiger-Müller counter connected to a "scale of 128"*. The counter had a mica window 1.25 in. in diameter and 2.1 mgm. per sq. cm. in thickness, and the aluminum disk was supported at a distance of 0.5 cm. from the window. A sufficient number of counts was recorded to ensure that the counting error was not greater than $\pm 1\%$. From the weight of the barium carbonate on the disk and the area over which it was spread, the thickness of the layer of barium carbonate was calculated in milligrams per square centimeter. The measured activity in the barium carbonate was then corrected to zero layer thickness by referring to a self-absorption curve (5). The activities of the various samples were calculated in terms of the number of counts per minute (extrapolated to zero layer thickness) per milligram of carbon present, and the activities of the prepared compounds were compared with that of the barium carbonate used as starting material on this basis. Each compound, except cyanamide, was crystallized to constant specific activity in order to remove any radioactivity due to traces of barium carbonate or carbon dioxide carried through the various procedures.

Nitrogen analyses were carried out using the micro-Kjeldahl procedure. All melting points were determined using a Fisher-Johns melting point apparatus.

Experimental

Cyanamide

Although it was pointed out by Franklin (4) that cyanamide could be prepared by passing dry ammonia over heated alkali carbonates, not many details were given of the method used. The following is an example of the

* *Nuclear Instrument & Chemical Corporation, Chicago, Ill.*

application of the procedure developed in the present investigation for the synthesis of radioactive cyanamide from radioactive barium carbonate.

Barium carbonate (3.11 gm.), giving 3165 counts per min. per mgm. of carbon, was weighed into a small platinum boat and the boat was placed in a quartz combustion tube in an electric furnace. Dry ammonia gas, prepared by warming concentrated ammonium hydroxide and passing the evolved gas first through a tube of soda lime and then through a tube containing sodium hydroxide pellets, was passed through the combustion tube. When the flow of ammonia had become rapid the combustion tube was heated to 850° C. and maintained at that temperature for three hours. The tube was then allowed to cool and the flow of ammonia was discontinued when the combustion tube reached room temperature. The platinum boat was removed from the tube and the fused contents was transferred to a small beaker and covered with 10 ml. of water. The mixture was cooled by immersion in an ice bath and stirred for 30 min. to break up any large lumps. An amount of ice-cold concentrated sulphuric acid equivalent to the barium present was then added dropwise and the mixture stirred for another hour. At intervals during this time the pH of the mixture was tested and, if the mixture had become alkaline, the pH was reduced to approximately 5.5 by the addition of hydrochloric acid. The mixture was centrifuged to remove as much of the solid material as possible and the supernatant liquid was transferred to a small round-bottomed flask. The precipitate in the centrifuge tube was washed several times with small volumes of water and the washings were added to the solution in the flask. This solution was then distilled to dryness under reduced pressure, care being taken not to allow the temperature of the contents to go above 40° C. The solid material that remained was extracted with several small portions of ether that were combined, the ether extract was evaporated to dryness, and the residue was then dried further *in vacuo* over phosphorus pentoxide. This residue was then extracted with dry ether and the crystalline material that remained after evaporation of the ether was dried *in vacuo* first over phosphorus pentoxide and then over sodium hydroxide pellets. The crystalline product weighed 487 mgm. (yield 73.5%) and melted at 40° C. Calc. for CH_2N_2 : C, 28.58; N, 66.62%. Found: C, 28.03, 28.05; N, 66.83%. Activity, 3075 counts per min. per mgm. C.

Because of the unstable nature of cyanamide it was not purified further but was used in other syntheses immediately after it was prepared.

Urea

Two methods were used to prepare urea labeled with C^{14} . In one method the compound was prepared from labeled cyanamide. In the second, urea was obtained from barium carbonate without first isolating the cyanamide, which occurs as an intermediate.

From Cyanamide.—Cyanamide (297 mgm.), having an activity of 3217 counts per min. per mgm. of carbon (prepared from barium carbonate with an activity of 3268 counts per min. per mgm. of carbon), was dissolved in

3 ml. of water and 0.5 ml. of concentrated hydrochloric acid. The solution was boiled under reflux for 10 min. then cooled and neutralized with sodium carbonate. The neutral solution was evaporated to dryness under reduced pressure and the residue was extracted with several small portions of boiling ethanol, which were combined. The ethanol extract was evaporated to dryness and the solid matter that remained was dried *in vacuo* over phosphorus pentoxide and then extracted with dry acetone in a micro-Soxhlet apparatus. The acetone was evaporated and the residue dried *in vacuo* over phosphorus pentoxide. The product weighed 388 mgm. (91% of theory; over-all yield from barium carbonate, 67%) and melted at 131° C. A mixture with an authentic sample of urea melted at 131° C. Calc. for CH_4N_2O : C, 20.00; N, 46.63%. Found: C, 20.19; N, 46.34%. Activity, 3244 counts per min. per mgm. C.

From Barium Carbonate.—Barium carbonate (3.10 gm.), having an activity of 3165 counts per min. per mgm. of carbon, was converted to cyanamide by the method already described. No attempt was made, however, to isolate the cyanamide. Instead, when the water extract had been distilled to dryness under reduced pressure, 3 ml. of water and 0.5 ml. of concentrated hydrochloric acid were added to the residue in the round-bottomed flask. The mixture was boiled under reflux for 10 min. and then cooled, neutralized, and evaporated to dryness. The residue was extracted as described in the preceding section to give 636 mgm. of urea (67.4% of theory) melting at 131° C. A mixture with authentic urea melted at 131.5° C. Calc. for CH_4N_2O : C, 20.00; N, 46.63%. Found: C, 20.20; N, 46.39%. Activity, 3101 counts per min. per mgm. C.

Thiourea

Thiourea was synthesized according to the method described by Plentl and Schoenheimer (6). Cyanamide (302 mgm.), with an activity of 3100 counts per min. per mgm. of carbon, was dissolved in 5 ml. of water and two drops of concentrated hydrochloric acid and 300 mgm. of antimony pentasulphide were added to the solution. A rapid stream of hydrogen sulphide was bubbled through the mixture while it was heated in a steam bath. This process was continued for two hours, after which time the mixture was boiled to remove excess hydrogen sulphide and filtered. The filtrate was neutralized with potassium carbonate and evaporated to dryness. The residue was crystallized twice from *n*-propanol to give 336 mgm. of thiourea (61.4% yield) melting at 174° C. A mixture with authentic thiourea melted at 174° C. Calc. for CH_4N_2S : C, 15.79; N, 36.82%. Found: C, 15.84; N, 36.38%. Activity, 3140 counts per min. per mgm. C.

Dicyandiamide

This compound was prepared by heating an aqueous solution of cyanamide in the presence of a small amount of ammonium hydroxide (1, 2, 8). Cyanamide (398 mgm.), with an activity of 2954 counts per min. per mgm. of carbon (prepared from barium carbonate with an activity of 2971 counts per min.

per mgm. of carbon), was dissolved in 4 ml. of water and 2 drops of concentrated ammonium hydroxide were added to the solution. The solution was boiled under reflux for four hours. It was then cooled and the crystals that separated out were collected on a sintered funnel and washed with several small portions of water that were added to the filtrate. A second crop of crystals was obtained by evaporating the filtrate to dryness and crystallizing the residue from water. A total yield of 350 mgm. of dicyandiamide (88% of theory) was obtained, m.p. 206°C . Calc. for $\text{C}_2\text{H}_4\text{N}_4$: C, 28.58; N, 66.62%. Found: C, 28.24, 28.28; N, 66.60%. Activity, 2966 counts per min. per mgm. C.

Guanidine Nitrate

The procedure employed for the preparation of guanidine nitrate was essentially that described by Davis (3). Dicyandiamide (405 mgm.), having an activity of 3246 counts per min. per mgm. of carbon, was weighed into a small, dry Pyrex test tube. Dry ammonium nitrate (900 mgm.) was added, the two materials were mixed thoroughly, and the mixture was then heated at 175° to 185°C . for three hours. During the period of heating, the mixture first melted to give a clear solution and then solidified. At the end of the heating period the contents of the test tube was cooled, dissolved in a small volume of warm water, and the solution was filtered to remove a small amount of insoluble material. The filtrate was evaporated to dryness and the residue crystallized from water. A further yield of crystals was obtained from the mother liquor. A total of 979 mgm. of guanidine nitrate (83% of theory) was obtained, m.p. 206°C . Calc. for $\text{CH}_6\text{N}_4\text{O}_3$: C, 9.84%. Found: 9.69%. Activity, 3286 counts per min. per mgm. C.

Acknowledgment

The authors are grateful to Miss Enid Anderson for assistance in the experimental work.

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THE ISOPIESTIC METHOD APPLIED TO SORPTION ISOTHERMS¹

By S. BARNARTT² AND J. B. FERGUSON

Abstract

The isopiestic method has been applied to the sorption of carbon tetrachloride and water vapors by activated coconut shell charcoals. The isopiestic charges were found to be linearly related over wide pressure ranges. Isotherms formed by plotting the isopiestic charges of two charcoals one against the other consisted of three linear sections for both carbon tetrachloride and water. If the pressure isotherm of one charcoal be known, those of other charcoals may be computed from it by weighing relatively few isopiestic charges. Errors inherent in the measurement of equilibrium pressures, as well as those caused by the drift of the pressure isotherms towards higher sorption capacities at a given pressure, are eliminated in the isopiestic method of comparing charcoals. The linear relation between the isopiestic charges affords a simple criterion of rejection for equations proposed to fit the pressure isotherms. It also throws into relief the structural regularities in activated charcoals. The existence of discontinuities in the sorption process, reported by previous experimenters, is supported by the isopiestic data.

Introduction

The isopiestic method, introduced by Bousfield (3) and subsequently improved by Sinclair (14) and by Robinson and Sinclair (10), has been extensively used to obtain the thermodynamic properties of aqueous solutions. Its use has been almost wholly confined to such studies, however, although it is a general method applicable to all equilibria involving the taking up (sorbing) of a substance (sorbate) by another phase (sorbent) in contact with it. In a previous report (13) it has been shown that the sorption capacities of activated charcoals towards vapors may be tested simply and rapidly using the isopiestic method. Nearly-saturated vapors were studied therein. The present report compares the activities of charcoals towards vapors over wide vapor pressure ranges.

The isopiestic method compares two or more sorbents by placing them in the liquid or gaseous phase containing the sorbate, and allowing the latter to distribute itself among the sorbents until equilibrium is established. The relative activity of each sorbent towards the sorbate is then given by the concentration of the latter in the sorbent. The activities of two or more charcoals towards a given vapor at a given pressure may be determined directly by simply weighing the charcoals before and after sorption. Such activities will hereinafter be termed "isopiestic charges", expressed as Q milligrams of sorbate per gram of sorbent.

The activity of a sorbent towards a vapor at a given temperature is commonly recorded by plotting the equilibrium charge against the vapor pressure. If one such isotherm be known, that of another sorbent may be obtained by measuring a number of sets of isopiestic charges.

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Isopiestic charges of two sorbents may also be plotted one against the other. We have called this type of plot "isotherm of isopiestic charges", abbreviated to IIC. To avoid confusion, the common isotherm of charge against vapor pressure will be called "pressure isotherm".

Each point on the IIC gives a direct comparison of the activities of two sorbents under identical conditions. For sorption by charcoals, therefore, it might be expected that the IIC would throw into relief any similarities in the surface or pore structures of the two charcoals. This paper describes experiments designed to study the character of IIC's for charcoals and to reveal what type of information they might supply. Sorption of carbon tetrachloride and water vapors was investigated.

Experimental

Isopiestic Charges

Isopiestic charges were determined by the following procedure. The charcoal samples in tared weighing bottles were heated to 125° C. for approximately 24 hr. After cooling in a closed desiccator for 15 min. the bottles were capped and weighed to obtain the "dry weights" of the samples.

The dried charcoals were placed in a vacuum desiccator with a sample of the sorbate liquid and the desiccator evacuated until all the air was swept out by the evaporating liquid. The system was then isolated and the sorbate vapor allowed to distill into the charcoals.

Sufficient sorbate was used to saturate the charcoals in order to remove by displacement the volatile impurities held on them. In this connection Allmand and Chaplin (1, 4) have shown that the removal of gaseous impurities from the charcoal surface is more effectively done by presaturation with carbon tetrachloride than by subjecting the charcoals to high temperature evacuation.

The saturated charcoals were next desorbed by evacuation until a suitable quantity of sorbate was removed. The desiccator was placed in an insulated box whose temperature varied by $\pm 1^\circ$ C. After one to five days, depending on the relative pressure P/P_s (where P is the equilibrium pressure and P_s the vapor pressure of the sorbate at the temperature in question), the equilibrium charges on the charcoals were measured by weighing. The minimum time necessary for the attainment of equilibrium was determined in preliminary experiments by finding the time required for duplicate samples of the same charcoal, initially one "dry" and the other laden with sorbate, to attain the same charge within the degree of inhomogeneity of the charcoal samples. Subsequent sets of equilibrium charges were secured either by further desorption or by allowing more sorbate to distill into the charcoals.

Pressure Isotherms for Carbon Tetrachloride

In order to correlate the IIC's with pressure isotherms it was necessary to obtain the pressure isotherms for the sorption of each vapor by one of the charcoals. In the case of carbon tetrachloride this was done simultaneously with the measurement of isopiestic charges, using the apparatus shown in

Fig. 1. This apparatus yielded pressure isotherms for carbon tetrachloride over the relative pressure range $P/P_s = 10^{-3}$ to $P/P_s = 10^{-1}$.

The apparatus fitted into and was supported by the ground-glass joint atop the vacuum desiccator. The pressure in the system was measured by means

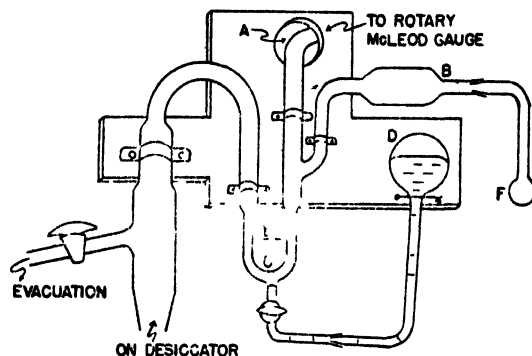


FIG. 1. Apparatus for measuring equilibrium pressures simultaneously with isopiestic charges.

of a rotary McLeod gauge reading from 0.0018 to 16 mm. of mercury. The gauge was positioned behind the wood support, the connecting tube being held tightly by the annular ring of rubber pressure tubing *A* inside the hole in the wood support. Tube *B* contained potassium hydroxide pellets for the removal of any carbon dioxide and water vapor from the vapor phase. The mercury cutoff *C* was operated by the small mercury reservoir *D* above which was a Torricellian vacuum. By swinging this reservoir down or up the cutoff was opened or closed.

When the pressure in the system became constant, a portion of the vapor phase was isolated by raising mercury to *E*. The carbon tetrachloride was frozen out by placing liquid air around bulb *F* and the residual pressure measured. In practice the residual pressures were small, ranging from 0.02 to 0.4 mm. of mercury. The total pressure of the vapor phase less the residual pressure gave the partial pressure of the carbon tetrachloride.

Pressure Isotherm for Water

The pressure isotherm for water was secured by isopiestic comparison of the charcoal with aqueous solutions. Sodium chloride solutions were used for the higher relative pressures, sulphuric acid solutions for the lower. Duplicate samples of the charcoal and of the solution were contained in four gold-plated silver dishes that were tapered to fit snugly into a silver-plated copper block inside the desiccator. This assembly and its application to isopiestic investigations has been described by Janis and Ferguson (8). The desiccator was evacuated carefully and allowed to rock gently in a water thermostat held at $25.0 (\pm 0.1)^\circ \text{C}$.

The relative pressures of the water vapor at equilibrium were obtained from the molality of the sodium chloride solutions using the activity data of Sheffer,

Janis, and Ferguson (12), and from the weight fraction of the sulphuric acid solutions using the activity data of Shankman and Gordon (11).

Materials Used

Charcoals: *A* was a steam activated coconut shell charcoal, impregnated with a catalyst.

B was an air activated coconut shell charcoal, impregnated with a catalyst.

C was an air activated coconut shell charcoal, impregnated with a catalyst.

D was an unimpregnated coconut shell charcoal.

Carbon tetrachloride. C.P. carbon tetrachloride, known to have methanol as chief impurity, was washed with water and distilled. $d_4^{25} = 1.592$.

Sodium chloride. "Kahlbaum Natriumchlorid 99.98%" was dried at 125° C. for two days. The dried product contained 0.2% water (Janis and Ferguson (8)).

Sulphuric acid. C.P. sulphuric acid was standardized by titration using anhydrous sodium carbonate (Analar "Analytical Reagent", purified by drying at 250° C. for 15 min.).

Results

Carbon Tetrachloride Isotherms

Isopiestic charges and simultaneous pressure measurements for charcoals *A* and *B* at 23° C. are presented in Table I, and the corresponding pressure isotherms in Fig. 2. Included also in the table are isopiestic charges outside the range of the measured pressure isotherms. All measurements are tabulated in chronological order.

The data within Groups I and III represent simple desorption points where the final operation on the system was evacuation of the charged charcoals, in the absence of free carbon tetrachloride liquid, until they were reduced to the charges shown. For Group II, however, the final operation was the distillation of carbon tetrachloride into the charcoals. In the latter procedure the carbon tetrachloride was frozen in bulb *F* (Fig. 1) using liquid air while the system was evacuated, then it was warmed and allowed to distill completely into the charcoals. Such determinations will be referred to as "adsorption" points.

Fig. 2 shows that these "adsorption" points all lay above the previous set of desorption points (Group I), indicating two distinct curves. The relative positions of the two curves, however, was the reverse of the usual adsorption-desorption hysteresis. Hence the charcoals have drifted towards higher activities at a given pressure, presumably a result of continuing evolution of gaseous impurities (1). The subsequent desorption points (Group III) confirmed the drift of the pressure isotherms, but indicated no further drift from

TABLE I

ISOPIESTIC SORPTION OF CARBON TETRACHLORIDE ON CHARCOALS *A* AND *B* AT 23° C.

Equilibrium pressure of CCl ₄ , <i>P</i> , mm. of mercury	<i>P/P</i> .*	Mgm. carbon tetrachloride per gram charcoal			
		<i>A</i>		<i>B</i>	
		Sample 1	Sample 2	Sample 1	Sample 2
<i>Group I</i>					
0.92	0.0088	499	514	539	544
0.54	0.0051	461	473	505	508
0.27	0.0026	422	430	468	470
0.13	0.0012	363	368	413	415
12.1	0.115	608	634	644	655
0.98	0.0093	491	504	533	538
9.09	0.0867	600	624	637	652
2.64	0.0251	548	569	590	594
3.38	0.0322	560	580	598	604
3.84	0.0366	563	583	602	608
0.075	0.00071	360	365	412	413
0.83	0.0079	483	497	528	533
<i>Group II</i>					
11.4	0.109	616	640	654	661
0.69	0.0066	490	503	534	538
2.22	0.0212	548	569	591	595
2.67	0.0254	560	580	599	605
3.79	0.0361	573	594	612	617
5.00	0.0476	583	601	621	626
10.4	0.0991	609	637	648	657
<i>Group III</i>					
1.27	0.0121	514	530	557	562
5.60	0.0534	588	610	626	633
6.42	0.0612	593	616	630	637
<i>Group IV</i>					
	1	690	727	757	760
	1	698	736	766	769
		667	698	731	742
		644	672	695	702
<i>Group V</i>					
		Sample 3	Sample 4	Sample 3	Sample 4
		135	137	165	161
		189	189	223	221
		222	223	261	259
		248	248	292	289

* *P_s* = 105 mm. of mercury (7).

TABLE I—*Concluded*ISOTHERMATIC SORPTION OF CARBON TETRACHLORIDE ON CHARCOALS A AND B AT 23° C.—*Concluded*

Equilibrium pressure of CCl ₄ , P , mm. of mercury	P/P_s *	Mgm. carbon tetrachloride per gram charcoal	
		A	B

Group VI

		Sample 5	Sample 6	Sample 5	Sample 6
		131	130	151	149
		298	292	342	343
		476	463	511	514
		Sample 7	Sample 8	Sample 7	Sample 8
		154	150	176	175
		196	190	226	226
		306	293	348	346
		511	487	540	538

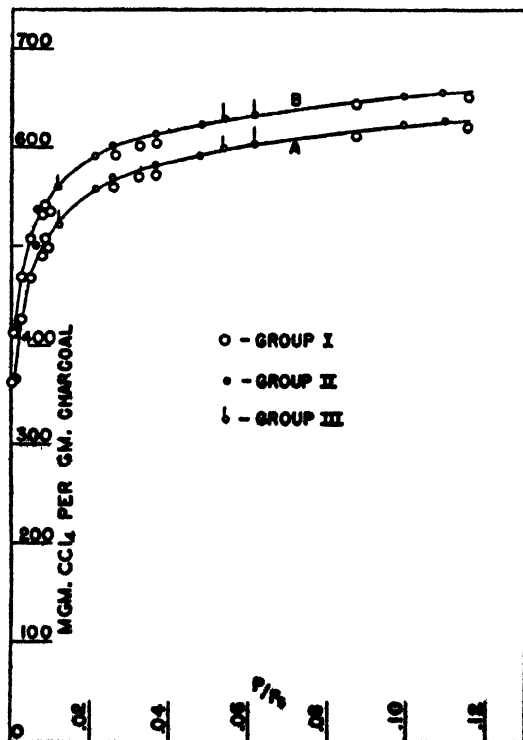
* P_s = 105 mm. of mercury (7).

FIG. 2. Pressure isotherms of carbon tetrachloride on charcoals A and B. 23° C.

Group II. The curves in Fig. 2 were therefore drawn to give preference to the points of Groups II and III.

The isopiestic charges of Table I are plotted as an isotherm of isopiestic charges in Fig. 3 (Curve I). The points of Group I are seen to lie on the same line as those of Groups II and III. Thus the IIC did not change as the pressure isotherms drifted towards higher activities at a given pressure.

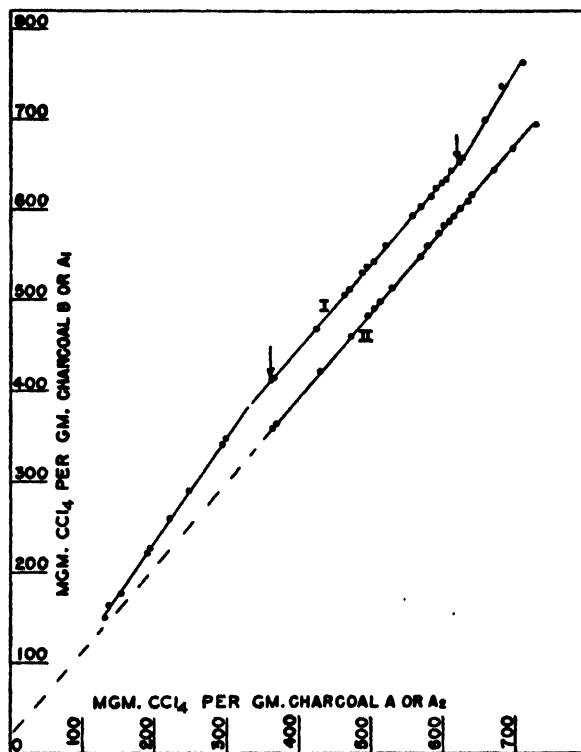


FIG. 3. Isotherms of isopiestic charges for the sorption of carbon tetrachloride by charcoals. 23° C. Curve I—Charcoals A and B. Curve II—"Duplicate" samples of charcoal A.

The low charges of Group V were obtained in the usual way except that the initial desorption of the presaturated charcoal samples was accelerated by heating the charcoals to 160° C. during the evacuation. Those of Group VI represent true adsorption points obtained by a continuous, slow distillation of carbon tetrachloride into charcoal samples that had not previously been exposed to it. The carbon tetrachloride was frozen in dry ice and allowed to distill *in vacuo* into the charcoal samples (at approximately 23° C.), the latter being weighed at intervals of one week. Since the distillation rate was minute, it was assumed that the charges on the charcoals at all times were the same as those for isopiestic equilibrium. This assumption is supported by the excellent agreement between Groups V and VI in Fig. 3. At very low pressures, therefore, true adsorption points yield the same IIC as desorption points.

As shown by Curve I, the IIC for the sorption of carbon tetrachloride by charcoals *A* and *B* can be represented accurately by three straight lines, over the pressure range from saturation down to an extremely minute value. The middle line includes the whole range of the measured pressure isotherms.

It should be noted that there was considerable inhomogeneity within each activated charcoal. The duplicate samples of charcoals *A* and *B* are seen from Table I to differ in activity by roughly 5% and 1% respectively as satu-

TABLE II

ISOPIESTIC CHARGES OF CARBON TETRACHLORIDE ON ACTIVATED CHARCOALS AT 23° C.
(Mgm. carbon tetrachloride per gram charcoal)

Charcoal C		Charcoal D		Charcoal B		Charcoal C
185		188		670		709
233		234		613		653
303		300		561		590
403		390		526		549
470		450		487		503
560		525		452		461
660		604		412		413
763		682				
774	Saturation	693				
774	Saturation	691				

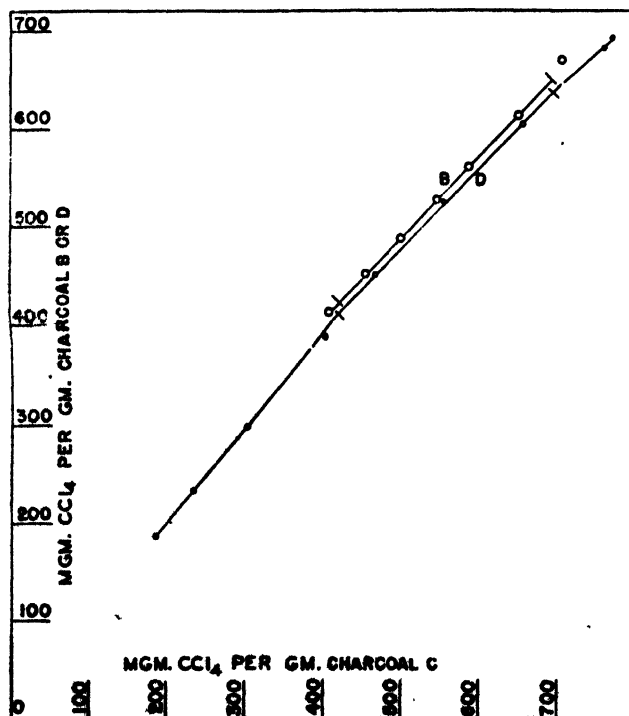


FIG. 4. Isotherms of isopiestic charges for the sorption of carbon tetrachloride, charcoals *B* and *D* vs. charcoal *C*. 23° C.

ration pressure is approached. This inhomogeneity was characteristic of all the charcoals studied, the duplicate samples exhibiting differences in activities ranging from 1% to 5%. The IIC for the duplicate samples of charcoal *A* is shown in Curve II, Fig. 3. Although these samples varied in activity by only 5% it was thought that the shape of the IIC would approximate that of two samples at different stages in the activation process. This IIC covers the pressure range from $P/P_s = 1$ down to $P/P_s = 0.0007$ and is a single straight line that extrapolates close to the origin.

Isopiestic charges of carbon tetrachloride on charcoals *B* and *C*, and *C* and *D*, are tabulated in Table II and plotted in Fig. 4. Over the range of the measured pressure isotherm for charcoal *B*, indicated by cross lines on each plot, both IIC's are linear. Theoretically, if the pressure isotherm of only charcoal *A* were known, those of *B*, *C*, and *D* could be computed after measuring as few as two sets of isopiestic charges within the pressure range in question.

Because of the linear relation between the isopiestic charges, the pressure isotherms of charcoals *C* and *D* will have the same general shape as those of charcoals *A* and *B* in Fig. 2.

Water Isotherms

The pressure isotherm for the sorption of water by charcoal *C* at 25.0° C. is presented in Table III and plotted in Fig. 5. Also shown in this figure is

TABLE III
PRESSURE ISOTHERM OF WATER ON CHARCOAL *C* AT 25.0° C.

Molality of NaCl solutions*	Weight fraction of H ₂ SO ₄ solutions*	P/P_s	Mgm. water per gram charcoal <i>C</i>		Time (days) allowed for equilibrium
			Sample 1	Sample 2	
3.18 6.145** 0.506		1	443	457	1
		0.885	411	426	16
		0.753	377	390	7
		0.983	428	441	16
	0.667	0.076	40	39	4
	0.545	0.259	56	55	4
	0.393	0.578	247	251	11
	0.528	0.291	77	76	3
	0.422	0.516	200	200	4

* Duplicate solutions agreed exactly to the third decimal place.

** Saturated solutions.

the pressure isotherm of charcoal *D*, obtained by isopiestic comparison with *C*. The isopiestic charges, Table IV, have been plotted as an IIC in Fig. 6.

Although the pressure isotherms for water differ so profoundly from those for carbon tetrachloride, the IIC's for these two sorbates are similar in that each may be represented by three straight lines.

TABLE IV

ISOPIESTIC CHARGES OF WATER ON ACTIVATED CHARCOALS AT 25° C.
(Mgm. water per gram charcoal)

Charcoal C	Charcoal D	Charcoal C	Charcoal D
15	17	315	308
61	39	207	179
105	58	149	105
140	92	91	64
360	344	426	394
380	363	224	214
		Saturation	

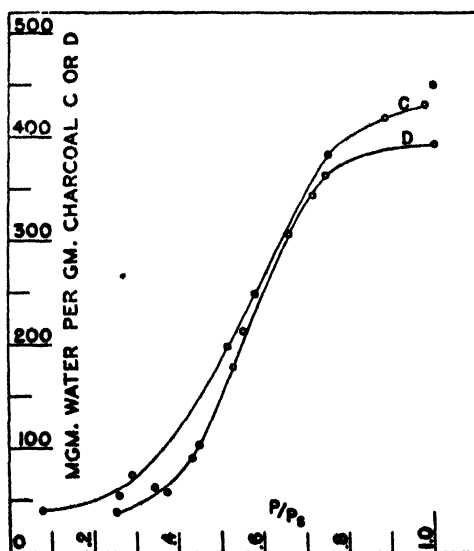


FIG. 5. Pressure isotherms of water on charcoals C and D. 25° C.

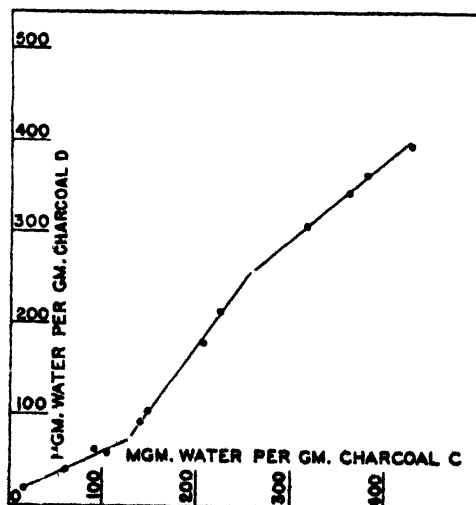


FIG. 6. Isotherm of isopiestic charges for the sorption of water by charcoals C and D. 25° C.

The isopiestic charges of the two samples of charcoal *C* in Table III are plotted as an IIC in Fig. 7. This IIC is seen to consist of two straight lines from zero charges to saturation. Thus, for water as for carbon tetrachloride, two samples of the same charcoal species have a simpler IIC than do two different charcoal species.

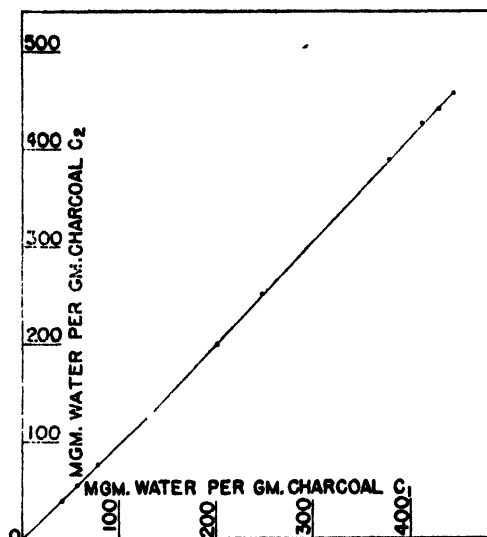


FIG. 7. Isotherm of isopiestic charges for the sorption of water by "duplicate" samples of charcoal *C*. 25.0° C.

Discussion

Discontinuous Sorption

The pressure isotherms obtained for the sorption of carbon tetrachloride by activated charcoals exhibit the same general shape as those that have been reported for carbon tetrachloride and many other vapors and gases (9, Chap. IV). A very careful investigation of the sorption of carbon tetrachloride at low pressures has been reported by Chaplin (4) and Allmand and Chaplin (1). At a carbon tetrachloride pressure of about 10^{-1} mm. and 25° C. (P/P_s of 0.00087), the pressure isotherms of their activated charcoals showed a discontinuous change with further increase in pressure. The heats of adsorption also showed a discontinuous change at about this pressure. The fact that the IIC's for our charcoals exhibit a discontinuity at a P/P_s just below 0.0007 substantiates the results of Allmand and Chaplin.

Further substantiation of this peculiarity is afforded by the data of Coolidge (5, 6). His typical isotherm for the sorption of an organic vapor by charcoal, plotted as Q vs. $\log P/P_s$, exhibits two points of inflection (6). The lower of these occurs at a P/P_s of roughly 10^{-3} , which is in agreement with the pressure isotherms of Allmand and Chaplin and with our IIC's. In addition, Coolidge's upper point of inflection occurs at a P/P_s of roughly 10^{-1} , which is in agreement with the upper discontinuity of our IIC's. It appears, therefore, that three equations would be required to describe the sorption of carbon tetrachloride by an activated charcoal over the whole pressure range.

Rejection Criterion

It has been shown that the IIC for the sorption of carbon tetrachloride by any pair of the four activated charcoals studied is a single straight line over the range of the measured pressure isotherm. This linear relation may be used as a criterion of rejection for equations proposed to fit the pressure isotherms. Let us propose, as an example, the Langmuir equation:

$$Q = \frac{aP}{1 + bP} \quad \text{or} \quad \frac{1}{P} = \frac{a}{Q} - b,$$

where a and b are constants. For isopiestic equilibrium between two charcoals Nos. 1 and 2, the Langmuir equation predicts that the reciprocals of the isopiestic charges are linearly related, since

$$\frac{1}{P} = \frac{a_1}{Q_1} - b_1 = \frac{a_2}{Q_2} - b_2.$$

This is not generally true if the isopiestic charges themselves are linearly related. In the special case where $b_1 = b_2$, however,

$$\frac{a_1}{Q_1} = \frac{a_2}{Q_2} \quad \text{or} \quad Q_1 = \frac{a_1}{a_2} \cdot Q_2,$$

and the IIC would be a straight line passing through the origin. Since our IIC's for carbon tetrachloride over the measured pressure range do not extrapolate through the origin, the Langmuir equation is mathematically inapplicable to our pressure isotherms. Similarly the Freundlich equation:

$$Q = c \cdot P^{1/n}$$

predicts that the logarithms of the isopiestic charges are linearly related and therefore is also inapplicable to our pressure isotherms. In confirmation, the four isotherms showed marked curvature when plotted either as $\frac{1}{P}$ vs. $\frac{1}{Q}$ or as $\log P$ vs. $\log Q$.

Theoretical Implications of Linear IIC's

Considering only the pressure range of the measured pressure isotherms for carbon tetrachloride, the following relations connect the isopiestic charges of the four charcoals studied:

$$Q_A = k_B + K_B \cdot Q_B = k_C + K_C \cdot Q_C = k_D + K_D \cdot Q_D,$$

where k 's and K 's are constants. It follows that

$$\frac{\Delta Q_A}{\Delta P} = K_B \cdot \frac{\Delta Q_B}{\Delta P} = K_C \cdot \frac{\Delta Q_C}{\Delta P} = K_D \cdot \frac{\Delta Q_D}{\Delta P}.$$

For a pressure increase from P to $P + \Delta P$, therefore, the corresponding increases in the charges on the four charcoals will be in the following proportions:

$$1 : \frac{1}{K_B} : \frac{1}{K_C} : \frac{1}{K_D} \dots$$

The above proportionality holds for any pressure increase ΔP , of any magnitude, within the range of the measured pressure isotherms. This would hardly be anticipated unless the same types of active surface were present in all four charcoals, each in the above-mentioned relative proportions.

The range of pressures over which this proportionality exists would be expected to be greater when comparing sorbents more closely related in composition and structure. Thus, two samples of a single charcoal species, prepared by the same activation process but activated to different extents, might exhibit a linear IIC over wider pressure ranges than do two of the different charcoal species studied here. In the limiting case where the activation process initially creates one or several types of active surfaces and then increases the concentrations of these uniformly without producing new types, one might anticipate IIC's that are single straight lines from zero pressure right up to saturation. Evidence, admittedly not very strong, that this limiting case may actually obtain in practice is afforded by Curve II, Fig. 3. This IIC, for two samples of the same charcoal species that differ in activity by about 5% at saturation, is one straight line from a P/P_s of 0.0007 up to saturation pressure and extrapolates close to the origin.

It is to be expected, therefore, that the IIC's for a series of charcoal samples representing the same starting material at different stages of an activation process would throw considerable light upon the activation mechanism. Such a series of charcoals has been investigated (2).

Conclusions

When the pressure isotherm for the sorption of a given vapor by one charcoal is known, the isopiestic method is an expedient means of obtaining the pressure isotherms of other charcoals. The existence of linear relations between the isopiestic charges, extending over wide pressure ranges, permits the computation of complete pressure isotherms by weighing relatively few isopiestic charges.

A comparison of the activities of two charcoals from individually measured pressure isotherms is subject to errors inherent in the measurement of equilibrium pressures and to errors caused by the drift towards higher charges at a given pressure. These inaccuracies are eliminated in the isopiestic method.

The linear relation between the isopiestic charges affords a simple criterion of rejection for equations proposed to fit the pressure isotherms. It also throws into relief the structural regularities in activated charcoals.

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AN ISOPIESTIC INVESTIGATION OF CHARCOAL ACTIVATION¹

BY S. BARNARTT² AND J. B. FERGUSON

Abstract

The isopiestic method was used to study the sorption of carbon tetrachloride, water, methanol, and toluene by a series of charcoals representing the same coconut shell source at different stages of steam activation. The sorption of water by two charcoals of this series impregnated with benzoic acid was similarly investigated. The isopiestic charges of this activation series of charcoals were linearly related over wider pressure ranges than were those of unrelated charcoals. The activation process was found to be connected primarily with the principal pressure range over which single straight lines were obtained on plotting the isopiestic charges one against the other. The isopiestic data presented the following picture of charcoal activation. The activation process has created surfaces, probably of a heterogeneous character, which are active to all the four vapors studied. At any stage of activation these surfaces take up proportionate quantities, but not equal liquid volumes, of each sorbate at saturation pressure. The various types of surfaces increase in abundance with activation at the same relative rate, so that they are always present in the charcoal in the same relative proportions, up to a certain stage of activation. At this stage the production of the surfaces active at relatively low pressures begins to decline. This indicates that new pores are being created more slowly in comparison with the widening of existing pores. In addition to the active surfaces just described, the activation process produces some chemically selective centers which are active at minute relative pressures. The water sorption data discredit the theory of capillary condensation.

Introduction

The application of the isopiestic method to the sorption of vapors by activated charcoals has been described (5). For conditions of isopiestic equilibrium, the "charges" (milligrams of sorbate per gram of sorbent) on two charcoals were found to be linearly related over wide pressure ranges. This linear relation revealed structural regularities in the two charcoals.

For the sorption of either carbon tetrachloride or water by two charcoals, the isotherm formed by plotting the isopiestic charges one against the other (termed "isotherm of isopiestic charges", abbreviated to IIC) was found to consist of three linear sections. The IIC's were even simpler for two samples of the same charcoal which had somewhat different activities. It was thought, therefore, that the IIC's for the sorption of vapors by a series of charcoals, representing the same starting material at different stages in the activation process, would yield information about the activation mechanism. This report deals with an isopiestic study of such a charcoal series.

The sorption of carbon tetrachloride and water vapors by the end member of this series (charcoal *D*) has already been reported (5). The IIC's comparing charcoal *D* with other charcoals not closely related to it were found to comprise three straight lines. Those comparing charcoal *D* with members

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of the activation series should have simpler construction if the linear relation between isopiestic charges reflects structural regularities in the charcoals.

Isopiestic sorption of carbon tetrachloride, water, methanol, and toluene vapors by the charcoal series has been investigated. The sorption of water by two charcoals of the series which were first impregnated with benzoic acid has also been studied. The IIC's for water, especially on charcoals whose internal structure has been modified, should provide a test for the validity of the controversial capillary condensation theory.

Experimental

Isopiestic Charges

Using the method previously described (5), samples of the whole series of charcoals were charged with sorbate and equilibrated simultaneously.

Impregnation with Benzoic Acid

Five grams of the dried, granular charcoal were stirred into 1 liter of benzoic acid solution containing 1 gm. of benzoic acid. After 24 hr. of occasional stirring, the supernatant liquid was decanted. The charcoal was washed twice with 20 ml. of distilled water, then dried at 125° C.

By this treatment some of the charcoal fines were lost on decantation, and a small amount of water was retained by the treated charcoals even after drying at 125° C. The total change in weight resulting from these two factors was determined by running a "blank" for each charcoal whereby distilled water replaced the benzoic acid solution. The "blank" charcoal accompanied the impregnated one in the isopiestic experiments.

Materials

(1) Benzoic acid—Kahlbaum's.

(2) Charcoals—The coconut shell charcoals *C* and *D* have been previously described (5). The latter was the end member of an activation series of charcoals: *D*1, *D*2, *D*3, *D*4, *D*5, *D*6, and *D*. Charcoals *D*1–*D*6 were samples removed from the steam activator at successive intervals during the activation of *D*. Charcoal *D* was nearly completely activated, i.e., further steam treatment would reduce its activity. Certain properties of this charcoal series are given in a recent paper by Lemieux and Morrison (10), who investigated the sorption of aliphatic acids from aqueous solutions. It should be noted that these authors designated the series by the numbers: 1, 2, 3, 5, 6, 7, and 8 respectively. Another member of the series which they designated charcoal 4 has been omitted by us because it proved to be practically identical with *D*4.

(3) Methanol—Absolute methanol was purified by the method of Lund and Bjerrum (11) to a purity of 99.8% by density.

(4) Toluene—B.D.H. "Certified Chemical" grade.

Results

Sorption of Carbon Tetrachloride

The isopiestic charges of carbon tetrachloride on the activation series of charcoals are tabulated in Table I. They are plotted as IIC's in Fig. 1 in

TABLE I
ISOPIESTIC CHARGES OF CARBON TETRACHLORIDE ON THE *D*-CHARCOALS AT 23° C.
(Mgm. carbon tetrachloride per gram charcoal)

<i>D</i> 1	<i>D</i> 2	<i>D</i> 3	<i>D</i> 4	<i>D</i> 5	<i>D</i> 6	<i>D</i>
32	60	81	124	169	182	188
39	73	98	149	204	223	234
47	88	120	184	252	280	300
55	105	144	224	312	350	390
62	116	160	250	348	396	450
68	129	178	279	392	449	525
75	144	199	312	438	506	604
92	171	230	357	491	566	682
*96	183	244	371	508	577	692

Saturation.

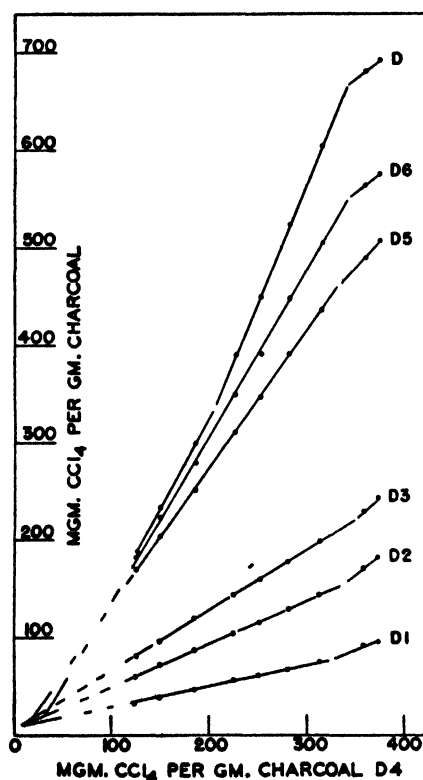


FIG. 1. Isotherms of isopiestic charges for the sorption of carbon tetrachloride by the activation series of charcoals. 23° C.

which each charcoal is compared to *D*4, the middle member of the series. Pressure isotherms for the charcoal series have been computed from Fig. 1 and the known (5) pressure isotherm for charcoal *D*. These are shown in Fig. 2.

The IIC's for the first six charcoals of the series are seen to be single straight lines from a low charge, representing a minute relative pressure, up to a charge representing a P/P_s of roughly 10^{-1} . These lines extrapolate approximately

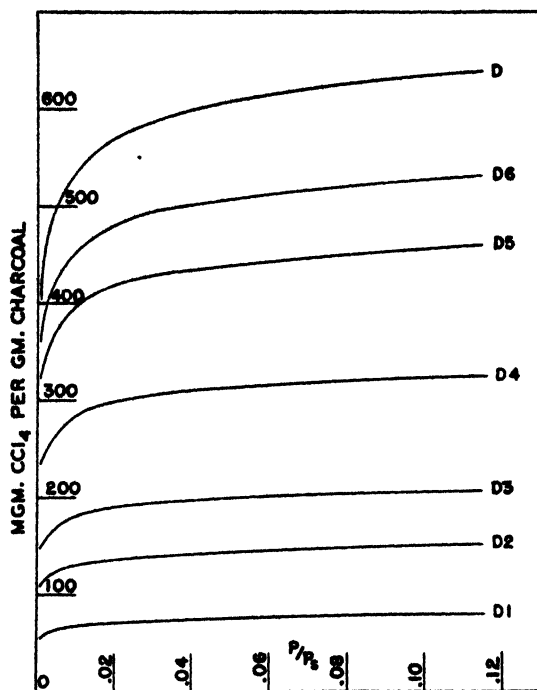


FIG. 2. Pressure isotherms of carbon tetrachloride on the activation series of charcoals. 23°C .

to a point close to the origin. The IIC for charcoal *D* compared with *D4*, and hence also if compared with any one of the first six charcoals of the series, contains a second discontinuity, thus resembling those previously reported for two "unrelated" charcoals (5).

Sorption of Water

The isopiestic charges of water on the series of charcoals are tabulated in Table II and plotted as IIC's in Fig. 3. Pressure isotherms for the charcoal series have been computed from Fig. 3 and the pressure isotherm for charcoal *D* (5). These are shown in Fig. 4.

The IIC's for the charcoal series are all composed of two linear portions, the lower one passing through the origin and the upper through saturation. Thus for water as for carbon tetrachloride, they are simpler than the IIC's of unrelated charcoals. The discontinuity in these IIC's occurs at charges that are approximately the points of inflection of the pressure isotherms. These charges represent roughly the same pressure, P^1 in Fig. 3, a relative pressure of 0.47. The lower line of each IIC is close to the 45° line; hence the activation process has produced little change in the activity of the charcoal over the P/P_s range 0 to 0.47.

The isopiestic data for the sorption of water by charcoals *D4* and *D6* impregnated with benzoic acid, and by the corresponding "blank" charcoals,

TABLE II
ISOPIESTIC CHARGES OF WATER ON THE *D*-CHARCOALS AT 25° C.
(Mgm. water per gram charcoal)

<i>D1</i>	<i>D2</i>	<i>D3</i>	<i>D4</i>	<i>D5</i>	<i>D6</i>	<i>D</i>
13	13	15	16	17	17	17
36	34	38	39	39	39	39
56	55	58	61	63	60	58
91	92	97	105	108	100	92
170	190	204	242	276	309	344
172	193	208	249	287	329	363
156	174	187	220	251	284	308
130	143	152	167	180	182	179
84	89	93	102	108	107	105
54	55	58	63	66	65	64
*183	206	221	266	307	354	394
132	145	156	176	197	210	214

* Saturation

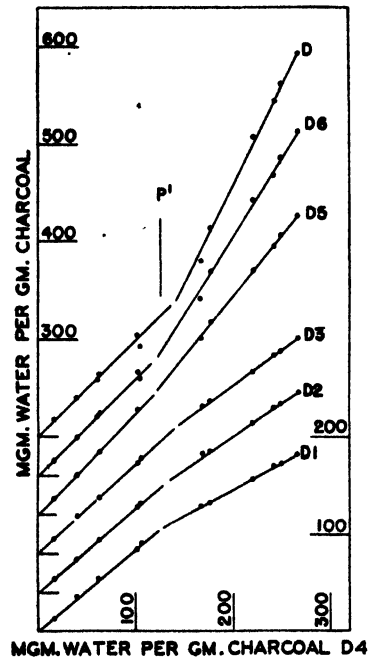


FIG. 3.

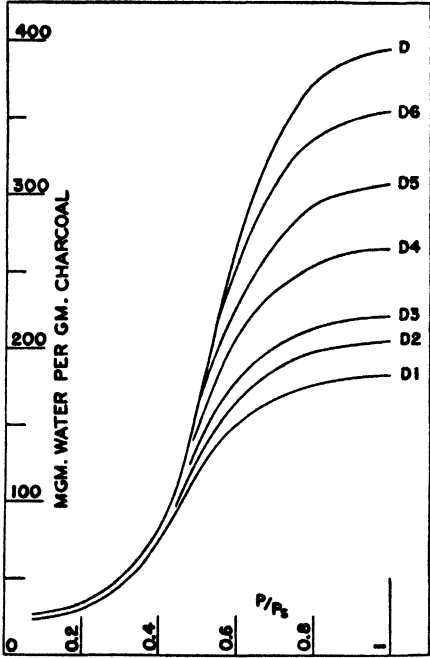


FIG. 4.

FIG. 3. Isotherms of isopiestic charges for the sorption of water by the activation series of charcoals. 25° C.

NOTE: For clarity the curves are separated by ordinate displacement. To obtain true ordinates:

Curve number	<i>D1</i>	<i>D2</i>	<i>D3</i>	<i>D5</i>	<i>D6</i>	<i>D</i>
Subtract from ordinate reading	0	40	80	120	160	200

FIG. 4. Pressure isotherms of water on the activation series of charcoals. 25° C.

TABLE III

ISOPIESTIC SORPTION OF WATER VAPOR BY CHARCOALS *D4* AND *D6*
 IMPREGNATED WITH BENZOIC ACID. 25° C.

P/P_s	Isopiestic charges, mgm. water per gram charcoal			
	<i>D4</i> impregnated	<i>D4</i> blank	<i>D6</i> impregnated	<i>D6</i> blank
1	177	277	258	359
0.79	163	260	236	338
0.77	161	257	233	332
0.64	128	212	174	258
0.57	114	177	140	200
0.55	109	155	131	167
0.50	91	112	102	108
0.46	83	93	90	87
0.345	46	46	46	42
—	15	12	15	12

are tabulated in Table III. The impregnation treatment resulted in the sorption of 117 mgm. benzoic acid per gram of charcoal *D4*, and 135 mgm. benzoic acid per gram of *D6*. The isopiestic charges of water on the impregnated charcoals shown in Table III were calculated as: (mgm. water)/(grams of impregnated charcoal less grams of benzoic acid thereon); hence all the charges for water refer to 1 gm. of dry unimpregnated charcoal.

The equilibrium pressures of Table III were given by samples of charcoal *C* equilibrated simultaneously. Pressure isotherms for the impregnated charcoals are shown in Fig. 5. They are similar in shape to those of Fig. 4, except

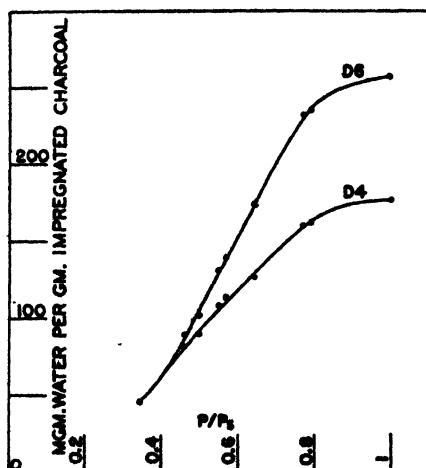


FIG. 5. Pressure isotherms of water on charcoals impregnated with benzoic acid. 25° C.

that the relatively rapid increase in sorption between $P/P_s = 0.45$ and $P/P_s = 0.65$ is somewhat more gradual. This is clearly evident from the IIC's in Fig. 6, the middle linear sections of which correspond to the relative

pressure range 0.45 to 0.65 and exhibit much greater sorption for the blank charcoals. Nevertheless the IIC comparing the two impregnated charcoals, shown in Fig. 7, is two straight lines from zero charge to saturation, the same as the IIC for the blanks.

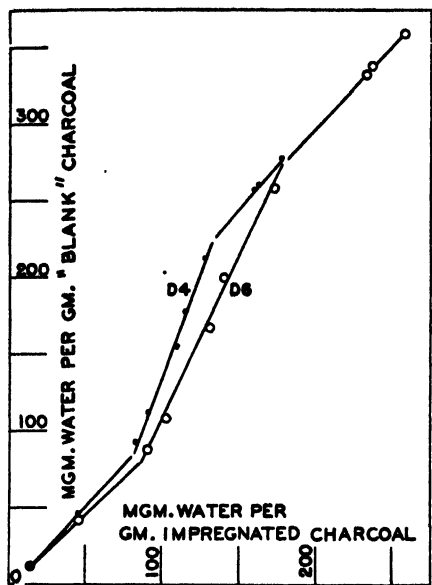


FIG. 6.

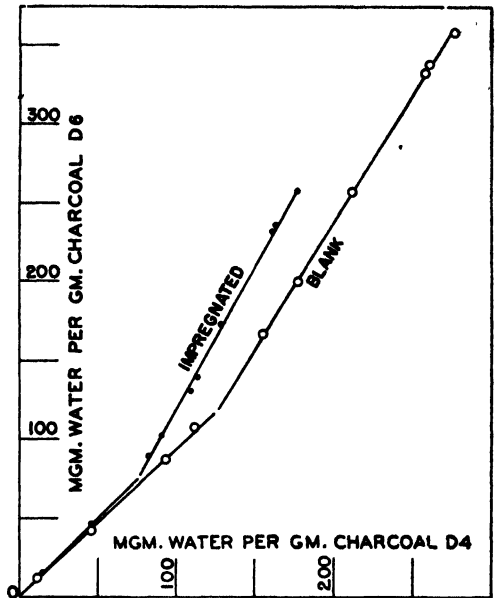


FIG. 7.

FIG. 6. Isotherms of isopiestic charges showing the effect of impregnating charcoals with benzoic acid on their water sorption. 25° C.

FIG. 7. Isotherms of isopiestic charges for the sorption of water by charcoals impregnated with benzoic acid and by the corresponding "blank" charcoals. 25° C.

Sorption of Methanol and Toluene

The isopiestic charges are tabulated in Tables IV and V and plotted as IIC's in Figs. 8 and 9. Samples of charcoal C were equilibrated with the

TABLE IV
ISOPIESTIC CHARGES OF METHANOL ON THE D-CHARCOALS AND CHARCOAL C AT 25° C.
(Mgm. methanol per gram charcoal)

D1	D2	D3	D4	D5	D6	D	C
*182	208	216	256	293	317	350	371
131	144	153	178	204	216	229	229
*183	202	205	240	285	316	357	380
136	150	160	190	218	231	246	251
158	175	187	229	270	296	331	354
129	142	149	171	191	198	206	208
100	106	108	112	117	116	113	112
82	86	87	87	87	84	81	83
63	64	64	62	60	58	56	65
111	121	125	136	145	146	145	144
*184	212	214	254	295	317	353	377
147	163	174	211	246	267	293	308

* Saturation.

TABLE V
ISOPIESTIC CHARGES OF TOLUENE ON THE D-CHARCOALS AND CHARCOAL C AT 25° C.
(Mgm. toluene per gram charcoal)

D1	D2	D3	D4	D5	D6	D	C
*109	144	192	253	310	344	398	414
105	138	184	242	295	326	374	386
102(.5)	133	177	230	280	308	352	361
101	131	173	222	269	296	336	345
** 95(.5)	123	161	204	243	264	291	298
** 87	112	144	178	205	219	233	239
** 84	108	137	167	191	202	212	220
** 77	100	125	150	165	175	179	189

* Saturation.

** Charcoal samples heated to 100° C. for one hour, then desorbed by evacuation while still hot.

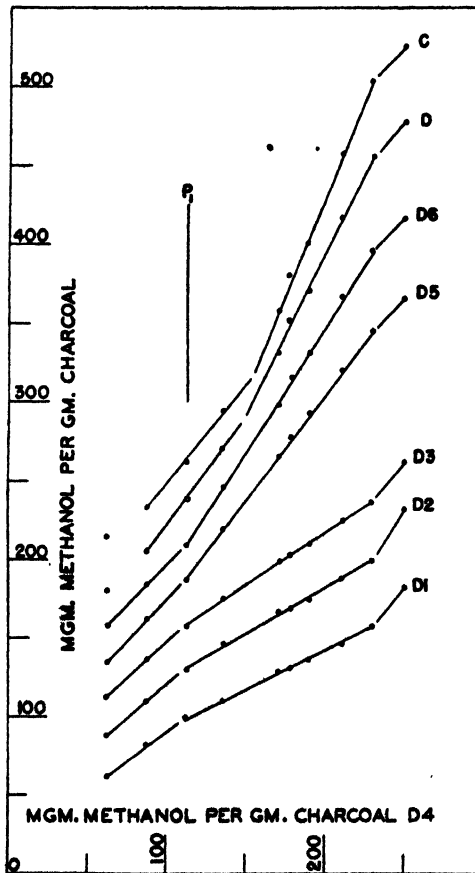


FIG. 8. Isotherms of isopiestic charges for the sorption of methanol by the activation series of charcoals. 25° C.

NOTE: For clarity the curves are separated by ordinate displacement. To obtain true ordinates:

Curve number	D1	D2	D3	D5	D6	D	C
Subtract from ordinate reading	0	25	50	75	100	125	150

activation series of charcoals since the former was the selected standard for isopiestic comparisons.* Here again the IIC's comprise linear sections and are simpler for any two of the charcoals *D1*–*D6* than for one of these compared with the unrelated charcoal *C*. Charcoal *D* behaves like an unrelated charcoal towards both methanol and toluene, as it did towards carbon tetrachloride.

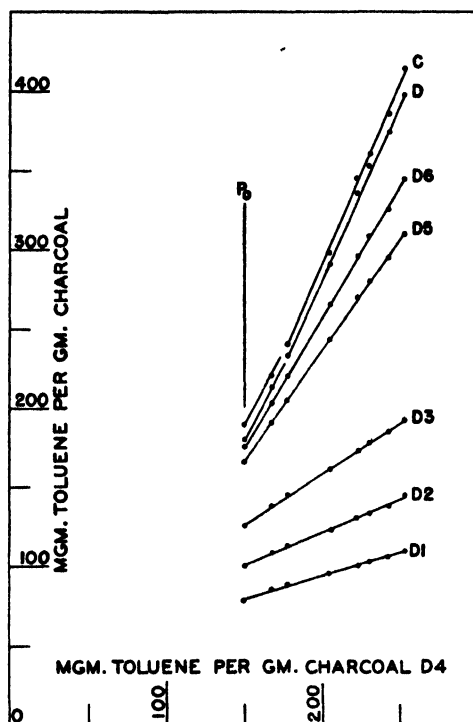


FIG. 9. Isotherms of isopiestic charges for the sorption of toluene by the activation series of charcoals. 25° C.

The IIC's for the sorption of toluene by charcoals *D1*–*D6* are the simplest for the four sorbates studied, being single straight lines from saturation pressure to a relative pressure (P_0 in Fig. 9) believed to be extremely small. This belief is based on the fact that the desorption of toluene by room temperature evacuation was very slow after the fourth set of isopiestic charges in Table V was obtained. The subsequent sets of isopiestic charges were determined by first heating the charged charcoals to 100° C. for one hour, then evacuating while still hot.

Discussion

Sorption of Water by the Activation Series

The pressure isotherms for water on the charcoal series resemble closely the desorption curves reported by Rakovsky (14) using blood charcoal, by Allmand and collaborators (1, 2, 3, 4) using wood and coconut shell charcoals,

* AUTHORS' NOTE: The pressure isotherms of methanol and toluene on the standard charcoal were determined in later experiments. These, and the pressure isotherms for the charcoal series computed from them, are more suitably reserved for a future report.

and by Coolidge (8) using coconut charcoal. The appreciable sorption at relative pressures below 0.3 reflects the presence of inorganic materials in the charcoals (2, 3, 4, 8), although the ash content was not determined. Water isotherms for an activation series of charcoals similar to ours have been reported by Fineman, Guest, and McIntosh (9). Although these were obtained by *adsorption* (condensation) rather than by desorption, the change in the curves as activation proceeds is roughly the same in both cases. The points of inflection of their curves are at approximately the same pressure, and at pressures below this value the activation process increased the activity of the charcoal very little.

The sorption of water by charcoals is often interpreted by the capillary condensation theory, in spite of serious anomalies reported by McBain, Porter, and Sessions (13). Fineman, Guest, and McIntosh, for example, have shown that the mean pore radius of a charcoal calculated from the water isotherm using the Cohan equation (7), assuming adsorption in annular rings, is in fair agreement with that computed from pore volume measurements using helium and mercury displacements plus surface area determinations by the method of Brunauer, Emmett, and Teller (6).

According to the capillary condensation hypothesis the capillaries of a given diameter will not sorb any water until a definite P/P_s is attained, at which P/P_s these capillaries become completely filled. The slope of the pressure isotherm at a certain P/P_s is therefore proportional to the amount of water that can be taken up by all the capillaries of the diameter corresponding to this P/P_s . Because of this correlation it is perhaps most convenient to define the "abundance of a given pore size" as being measured by the total volume of all capillaries of the given diameter, since the volume is directly proportional to the slope of the water isotherm. This definition will be used throughout the following discussion.

The most abundant pore size in the charcoal is that corresponding to the maximum slope of the pressure isotherm, i.e., to the point of inflection. The points of inflection for the activation series of charcoals occurred at approximately the same P/P_s , hence the most abundant pore size is not changed by activation from the state of charcoal *D1* to that of *D*.

The lower lines of the IIC's for the charcoal series, corresponding to the P/P_s range 0 to 0.47, are concerned with condensation of water into capillaries smaller than the most abundant size. Some of the sorption encompassed by the lower lines, however, may be on the inorganic ash in the charcoal. The latter type of sorption should be independent of activation. The lower line for any two charcoals of the series approximates the 45° line, i.e., all the sorption over the P/P_s range 0 to 0.47 is practically independent of activation. Hence the abundance of all capillaries smaller than the most abundant size remains roughly unchanged during the activation process.

The upper linear portions of the IIC's corresponding to the P/P_s range 0.47 to unity, are concerned with capillaries larger than the most abundant size. For these larger capillaries it follows (5) that:

$$\frac{\Delta Q_{D1}}{\Delta P/P_s} = K_{D2} \cdot \frac{\Delta Q_{D2}}{\Delta P/P_s} = K_{D3} \cdot \frac{\Delta Q_{D3}}{\Delta P/P_s} = \dots \text{etc.}$$

where the K 's are constants independent of capillary size.

$$\text{As } \Delta P/P_s \rightarrow 0: \frac{\partial Q_{D1}}{\partial P/P_s} = K_{D2} \cdot \frac{\partial Q_{D2}}{\partial P/P_s} = K_{D3} \cdot \frac{\partial Q_{D3}}{\partial P/P_s} = \dots \text{etc.}$$

Replacing $\frac{\partial Q}{\partial P/P_s}$ by A , the abundance of the pore size corresponding to the P/P_s in question as heretofore defined, then:

$$A_{D1} = K_{D2} \cdot A_{D2} = K_{D3} \cdot A_{D3} = \dots \text{etc.}$$

Since charcoals $D2$, $D3$, $D4 \dots$ represent progressively longer activations of the initial charcoal $D1$, the above equations may be condensed to the general form: $A'_i = K \cdot A_i^0$, where A'_i is the abundance of the pore size i at Stage ' of the activation process, A_i^0 is the abundance of this pore size at the initial activation stage, and K is a constant independent of pore size and dependent upon the time of activation.

Thus the application of the capillary condensation hypothesis to the water sorption data yields the following picture of the activation process. There is a certain pore size which remains more abundant than any other size throughout the activation process. Considering any pore size smaller than the most abundant size, the rate of production is practically the same as the rate of enlargement, so that this pore size retains practically the same abundance throughout the activation process. For any pore size larger than the most abundant size, the rate of production continually exceeds the rate of enlargement and the abundance increases with activation. All such larger pore sizes, however, increase in abundance at the same relative rate, according to the condition: $A'_i = K \cdot A_i^0$.

Sorption by Charcoals Impregnated with Benzoic Acid

The charcoals impregnated with benzoic acid exhibit a marked decrease in the saturation charges for water. Applying the capillary condensation hypothesis, the saturation volume of water on an impregnated charcoal should be less than that on the corresponding blank charcoal by an amount equal to the volume of benzoic acid. Table VI shows that this is true for both the charcoals which were impregnated with benzoic acid. The volumes given in this table were calculated assuming the densities of water and benzoic acid on the charcoals to be the same as those of the pure substances.

The location of the benzoic acid in the charcoals may be gleaned from the IIC's of Fig. 6, which compare the impregnated charcoals with the corresponding blanks. The lowest linear portions of these IIC's resemble the lower portions of the IIC's for the activation series in that they cover the P/P_s range 0 to 0.45, practically the same range as the latter, and approximate

TABLE VI

VOLUMES OF SORBED WATER AND BENZOIC ACID ON CHARCOALS *D4* AND *D6*. 25° C.

<i>P/P_s</i>	Volume (cc.) on 100 gm. of charcoal:							
	<i>D4</i> impregnated			<i>D4</i> blank	<i>D6</i> impregnated			<i>D6</i> blank
	Benzoic acid	Water	Total	Water	Benzoic acid	Water	Total	Water
1	0.093	0.176	0.269	0.276	0.107	0.256	0.363	0.358
0.79	0.093	0.162	0.255	0.259	0.107	0.235	0.342	0.337
0.77	0.093	0.160	0.253	0.256	0.107	0.232	0.339	0.331
0.64	0.093	0.128	0.221	0.211	0.107	0.173	0.280	0.257
0.57	0.093	0.114	0.207	0.176	0.107	0.139	0.246	0.199
0.55	0.093	0.109	0.202	0.154	0.107	0.131	0.238	0.166
0.50	0.093	0.091	0.184	0.112	0.107	0.102	0.209	0.108
0.46	0.093	0.083	0.176	0.093	0.107	0.090	0.197	0.087
0.345	0.093	0.046	0.139	0.046	0.107	0.046	0.153	0.042
—	0.093	0.015	0.108	0.012	0.107	0.015	0.122	0.012

the 45° line. Thus impregnation with benzoic acid also has not appreciably changed the sorption by capillaries smaller than the most abundant size. Over the middle linear portions of the IIC's in Fig. 6, corresponding to the *P/P_s* range 0.45 to 0.65 for both charcoals, the blank charcoals exhibit considerably larger sorption than do the impregnated ones. Over this *P/P_s* range, impregnated charcoal *D4* has sorbed 0.091 ml. per gm. more water than blank *D4*, and impregnated *D6* has sorbed 0.105 ml. per gm. more than Blank *D6*. These values are in good agreement with the concentrations of benzoic acid on the impregnated charcoals viz., 0.093 and 0.107 ml. per gm. on *D4* and *D6* respectively. The benzoic acid is therefore all situated in pores which, before impregnation, were within the size range that filled with water at *P/P_s* values between 0.45 and 0.65.

Considering only this range of pore sizes, the linear IIC's of Fig. 6 may be described by the equation: $A_i^I = K^I \cdot A_i$, where A_i^I is the abundance of pore size *i* in the impregnated charcoal, A_i is its abundance in the blank charcoal, and K^I is a constant descriptive of the charcoal and independent of pore size. Thus the capillary condensation hypothesis leads to the following conclusions:

1. Benzoic acid has been taken up in such a manner that each pore size within the range in question is reduced in abundance by the same factor, K^I .

2. The abundance of pores larger or smaller than the size range in question has not been appreciably changed, i.e., no such larger or smaller pores have been created by the presence of benzoic acid. Consequently a fraction, $1 - K^I$, of each pore size within the range in question must have been filled or otherwise made inactive by the benzoic acid sorption.

These conclusions are inconceivable from the standpoint of any of the common theories applicable to the sorption of benzoic acid by charcoal. It may be stated, therefore, that the isopiestic water sorption data discredit the theory of capillary condensation.

Mechanism of Activation

The saturation charges for the four sorbates studied were converted to volumes using the density of the pure liquid. These saturation volumes, V_s , are plotted in Fig. 10, one sorbate against another with carbon tetrachloride as reference. They are linearly related for all four sorbates, i.e. if ΔV_s is the increase in sorption capacity during any given activation interval:

$$(\Delta V_s)_{\text{CCl}_4} = a \cdot (\Delta V_s)_{\text{water}} = b \cdot (\Delta V_s)_{\text{methanol}} = c \cdot (\Delta V_s)_{\text{toluene}}.$$

In other words an increase in the activity of the charcoal towards any one of the sorbates is always accompanied by proportionate increases in its activity towards the other sorbates.

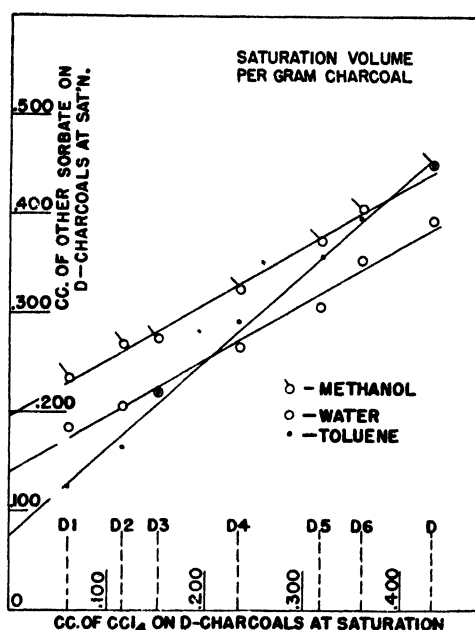


FIG. 10. Liquid volumes sorbed on the activation series of charcoals at saturation pressure.

Since the constants a , b , and c above are not unity, the new active centers created by the activation process do not sorb equal volumes of all four sorbate liquids at saturation. It would be expected, therefore, that the "Liquid Rule", which states that equal volumes of liquids are sorbed as the P/P_s of the vapor approaches unity, will not hold for activated charcoal at any stage in the activation process. The evidence in support of the Liquid Rule, summarized by McBain (12, pages 135-140), may be considered fortuitous, although one might expect the rule to hold when restricted to sorbates having similar molecular structures.

Fig. 10 has shown that any activation interval resulted in proportionate increases in charcoal activity for all four sorbates studied. Therefore the same active surfaces must be concerned with the sorption of each vapor. The IIC's supply information concerning the distribution of these active surfaces.

Fig. 3 showed that the IIC's for the sorption of water by the charcoal series each consisted of two straight lines. The lower lines all approached the 45° line, hence the activation process is concerned almost entirely with the upper lines of the IIC's. Similarly for the sorption of methanol and carbon tetrachloride, the activation process from stage *D1* to stage *D6* is concerned almost exclusively with the principal linear section of each IIC, since the lines above and/or below this section always approach the 45° line. Furthermore the principal lines cover practically the same P/P_s range independent of the activation state of the charcoal; this P/P_s range, however, is different for each sorbate. Thus the IIC's are single straight lines over the P/P_s range to which the charcoal becomes activated.

The mathematical significance of this, following the same reasoning as used above for the capillary condensation hypothesis but omitting all assumptions about the sorption mechanism, is given by the equation: $A_1 = k \cdot A_2$, where A , the activity at a given P/P_s , $\equiv \frac{\partial Q}{\partial P/P_s}$, the slope of the pressure isotherm at this P/P_s ; subscripts 1 and 2 refer to two stages of activation; and k is a constant independent of P/P_s but dependent upon the sorbate and the two activation stages considered.

This equation will be considered in the light of both homogeneous and heterogeneous surfaces, since the degree of heterogeneity in charcoals has never been firmly established. If, as assumed by the Langmuir theory of monomolecular adsorption, the active charcoal surface is homogeneous, then either all the pores have the same diameter and composition, or the surface inside the smaller pores has the same activity per unit area at any given P/P_s as does the surface inside the larger ones. In either case the above equation would apply, since the activity at any P/P_s would be directly proportional to the total active surface area.

If, on the other hand, the active charcoal surface is heterogeneous, the pores probably vary over a wide range of sizes and exhibit different activities per unit area at a given P/P_s . Local active centers may exist within the pores. Applying the above equation to such heterogeneous surfaces, the various types of active surfaces created by the activation process must be present in the charcoal in the same relative proportions at any stage of the activation process from *D1* to *D6*.

Although these considerations have been derived from the data for water, carbon tetrachloride and methanol, they apply also to the toluene data over the whole P/P_s range of the measured IIC's. The IIC's for toluene, however, do not extrapolate even roughly to a single point on the 45° line. Thus the activation process has created active centers in the charcoal which sorb toluene below the P/P_s at which the IIC's become discontinuous. This P/P_s is even more minute than the value represented by P_0 in Fig. 9, which suggests that the surfaces active below the discontinuity pressure function by chemical combination rather than by adsorption.

The IIC's for toluene, carbon tetrachloride, and methanol exhibit an additional discontinuity in the case of charcoal *D*. For each sorbate this occurs near the low pressure end of the principal linear section of the IIC. When activation has progressed to the stage of charcoal *D*, therefore, the surfaces active at the lower pressures are being produced relatively more slowly. Since such surfaces would be associated primarily with the smaller pores, the activation process at this stage is producing new pores more slowly in comparison with the widening of existing pores. The additional discontinuity at the stage of charcoal *D* is not evident in the IIC's for water (Fig. 3.); the water data, however, are considered inconclusive with respect to the absence of this discontinuity.

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

I. STATISTICS OF NETWORK POLYMERS¹

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Abstract

Theoretical treatments of the elastic and swelling properties of three-dimensional polymers are reviewed and the predicted influence of network structure discussed. An expression is obtained for the statistically most probable distribution of molecular weight for polymers terminated by chain transfer with a modifier. Depletion of modifier does not lead to a large increase in molecular heterogeneity. The formation of an insoluble fraction and the development of cyclic structures when such polymers are subjected to cross-linking conditions are treated by an application of the theory of gelation.

The peculiar mechanical properties of vulcanized rubber and certain other polymeric materials are generally ascribed to a three-dimensional network structure resulting from the presence of occasional cross-linkages between long chain-like molecules. Rubberlike elasticity has received extensive theoretical treatment, but experimental support for the theories has been comparatively meager. The course of a cross-linking reaction is difficult to follow since gelation intervenes after a small amount of reaction has occurred and makes analysis of the product difficult. Moreover, structural changes during vulcanization may be difficult to interpret if degradation accompanies cross-linking as a result of the rather drastic conditions generally employed.

It has been found in this laboratory that such difficulties are largely circumvented if the cross-linking reaction takes place in an emulsion of the polymer. In the investigations to be discussed in subsequent papers, the copolymer of butadiene and styrene (GR-S) was cross-linked at relatively low temperatures by addition of potassium persulphate to monomer-free latex.

In this first paper is presented an outline of relevant aspects of the statistical theory of three-dimensional polymers together with certain extensions of the theory that are required for interpretation of the experimental results.

Elasticity

It is now generally recognized that the retractive force in stretched rubber arises from thermal motions of the structural units rather than from attractive forces or deformation of valence angles. When rubber is stretched the long

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chains that make up its structure are forced into less random states. The deformation is therefore accompanied by a decrease of entropy. Measurements of the thermoelastic properties of rubber (1, 27, 29, 43) have shown that the major part of the retractive force is associated with the increase of entropy accompanying return to the more random (unstretched) state.

Proceeding from this viewpoint, a number of workers have derived expressions for the theoretical retractive force in terms of the elongation and the network structure. The "equation of state" for flexible polymer networks has been expressed (14, 21, 25, 36, 40) in the form:

$$\tau = \frac{\nu}{V} RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) \quad (1)$$

τ = tension (force per unit area of initial cross section),

R = gas constant,

T = absolute temperature,

l = stretched length,

l_0 = unstretched length,

$\frac{\nu}{V}$ is a proportionality constant characteristic of the rubber sample and dependent on structure. It will henceforth be called the "network activity."

The deduced dependence of retractive force on temperature and elongation agrees with experimental thermoelastic properties (1, 27, 29) and stress-strain curves (1, 9, 29, 37, 44) for various rubberlike polymers. On the other hand elasticity theories do not agree on the exact dependence of the proportionality constant $\frac{\nu}{V}$ on network structure. In several of the theories this quantity is proportional to the number of "chains" per unit volume where the "chain" is defined as the part of a molecule extending from one cross-linkage to the next. For an ideal network formed from indefinitely long molecules, the number of chains is identical with the number of cross-linked monomer units or equal to twice the number of cross-linkages. If a fraction ρ of the structural units is involved in cross-linkages, the concentration of chains (moles per cubic centimeter) is $\frac{d}{M_0} \rho$ and the theoretical relation between network activity and degree of cross-linking is given by:

$$\frac{\nu}{V} = g \frac{d}{M_0} \rho \quad (2)$$

d = density of the polymer (grams per cubic centimeter),

M_0 = molecular weight of the structural unit.

The proportionality constant, g , is unity in the theories developed by Wall (39, 40, 41), Treloar (36), and Flory and Rehner (14). Kuhn (24, 25) believes

that vulcanized rubber contains "steric junction points" in addition to chemical cross-linkages, and has arrived at a theoretical value of $\frac{7}{3}$ for g . James and Guth (22) conclude that g should be above $1/2$.

Flory has taken into account the molecular weight of the polymer before cross-linking (9, 11). Each "primary molecule" is considered to give rise to two inactive terminal chains in the vulcanizate, thereby leading to an "effective" degree of cross-linking of $\rho - \frac{2}{\bar{y}_n}$ where \bar{y}_n is the number average degree of polymerization prior to cross-linking. Equation (2) may then be modified to:

$$\frac{\nu}{V} = g \frac{d}{M_0} \left(\rho - \frac{2}{\bar{y}_n} \right). \quad (3)$$

Experiments with close-cut fractions of butyl rubber confirmed the validity of this correction for initial molecular weight, but failed to support the theoretical proportionality between network activity and degree of cross-linking (9, 11). Experimental values of g were 3.3 for $\rho = 1.6 \times 10^{-3}$ and 2.1 for $\rho = 2.8 \times 10^{-3}$. Flory has suggested that the discrepancy between theory and experiment results from entanglements within the network which restrict chain configurations and so augment the retractive force.

Swelling

Polymers possessing a network structure swell when placed in suitable liquids. Flory and Rehner (15) have developed a thermodynamic treatment of the swelling phenomenon which relates equilibrium swelling volume and network activity $\left(\frac{\nu}{V} \right)$:

$$\frac{\nu}{V} = \frac{\ln(1 - v_2) + v_2 + \mu_g v_2^2}{-V_1 v_2^{1/3}}, \quad (4)$$

v_2 = volume fraction of polymer in the swollen gel in equilibrium with pure solvent; i.e., the reciprocal of the "swelling volume" (ratio of the volumes of swollen and dried gel),

μ_g = solvent-polymer interaction coefficient (10, 19),

V_1 = molar volume of solvent.

For large swelling (v_2 small), Equation (4) reduces to the approximate expression

$$\frac{\nu}{V} \doteq \frac{(1 - 2\mu_g) v_2^{5/3}}{2 V_1}. \quad (5)$$

Combining Equations (1) and (5), the relation between tension and equilibrium swelling volume is:

$$\tau \doteq \frac{RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) (1 - 2\mu_g) v_2^{5/3}}{2 V_1}, \quad (6)$$

i.e., the tension at a given elongation should be inversely proportional to the 5/3 power of the swelling volume. Butyl rubber swollen in cyclohexane has been shown to conform to this relation (9).

Primary Molecular Size Distribution

Prior to cross-linking, polymeric molecules possess a distribution of molecular size, which is the statistical result of the random occurrence of termination steps during chain growth. If the probability that a growing molecule adds an additional monomer unit is represented by p then the distribution of primary molecular size of the resulting polymer (4, 31) is given by:

$$W_v = y (1 - p)^2 p^{y-1}, \quad (7)$$

W_v = weight fraction of species containing y structural units.

The above distribution has been discussed by several workers (4, 18, 30, 31) who have shown that the following relations exist.

The "number average" value of y

$$\bar{y}_n = \frac{1}{1 - p}.$$

The "weight average" value of y

$$\bar{y}_w = \frac{1 + p}{1 - p}.$$

The "heterogeneity index"

$$\frac{\bar{y}_w}{\bar{y}_n} = 1 + p \doteq 2,$$

since if a high polymer is to result p must be close to unity.

The "viscosity heterogeneity index"

$$\frac{\bar{y}_v}{\bar{y}_n} \doteq \{\Gamma (2 + a)\}^{1/a},$$

where a is the empirical coefficient (8, 20) in the relation between intrinsic viscosity (η) and degree of polymerization*

$$(\eta) = K \bar{y}_v^a.$$

The foregoing relations will now be employed to discuss the primary molecular size distribution in polymers such as GR-S formed in the presence of a chain transfer agent (modifier). Since abundant evidence (23, 32, 33, 42) indicates that here the main termination mechanism is transfer with the modifier, the probability (or rate) of termination relative to propagation may

* For GR-S dissolved in benzene or toluene (16) a has the value of 0.67, and the theoretical viscosity heterogeneity index at low conversion is about 1.85. Measurements by Harris and Kolthoff with GR-S of 5% conversion give an average value of 1.84 ± 0.09 (17), thereby providing partial confirmation for the distribution represented by Equation (7).

be taken equal to the rate of modifier disappearance relative to conversion. The latter is generally first order with respect to conversion up to at least 50% yield (3, 28), i.e.,

$$\frac{1-p}{p} = -\frac{dR}{d\alpha} = rR \quad (8)$$

R = modifier concentration (as moles per mole of initial monomer),

α = fractional conversion,

r = "regulating index" (3).

Since p is very close to unity, the above equation may be replaced by:

$$1-p \doteq rR. \quad (9)$$

In general p varies as conversion proceeds. The cumulative distribution at conversion α_1 is then

$$\begin{aligned} W_{\alpha_1} &= \frac{1}{\alpha_1} \int_0^{\alpha_1} W_{\alpha} d\alpha \\ &= \frac{1}{\alpha_1} \int_0^{\alpha_1} y (1-p)^2 p^{y-1} d\alpha. \end{aligned}$$

From Equations (8) and (9)

$$d\alpha = \frac{dp}{r(1-p)}.$$

$$\begin{aligned} \text{Hence } W_{\alpha_1} &= \frac{1}{r\alpha_1} \int_{p_0}^{p_1} y (1-p) p^{y-1} dp \\ &= \frac{1}{r\alpha_1} \left\{ p_1^y \left(1 - \frac{y}{y+1} p_1 \right) - p_0^y \left(1 - \frac{y}{y+1} p_0 \right) \right\}. \end{aligned} \quad (10)$$

p_0 and p_1 are the values of the parameter at conversions zero and α_1 , respectively.

The "number average" value of y at conversion α_1 is given by:

$$\begin{aligned} \bar{y}_{n\alpha_1} &= \frac{\text{Moles of monomer polymerized}}{\text{Moles of modifier consumed}}, \\ &= \frac{\alpha_1}{R_0 - R_1}. \end{aligned} \quad (11)$$

R_0 and R_1 are the modifier concentrations (as defined above) initially and at conversion α_1 , respectively.

Integrating Equation (8)

$$R_1 = R_0 e^{-r\alpha_1}. \quad (12)$$

$$\bar{y}_{n\alpha_1} = \frac{\alpha_1}{R_0 (1 - e^{-r\alpha_1})}. \quad (13)$$

The "weight average" value of y at conversion α_1 is given by:

$$\begin{aligned}\bar{y}_{w\alpha_1} &= \frac{1}{\alpha_1} \int_0^{\alpha_1} \bar{y}_w d\alpha \\ &= \frac{2}{r\alpha_1} \int_{p_0}^{p_1} \frac{dp}{(1-p)^2} \\ &= \frac{2}{r\alpha_1} \left(\frac{1}{1-p_1} - \frac{1}{1-p_0} \right) \\ &= \frac{2}{r^2\alpha_1} \left(\frac{1}{R_1} - \frac{1}{R_0} \right) \\ &= \frac{2}{r^2\alpha_1 R_0} (e^{r\alpha_1} - 1) .\end{aligned}$$

Hence the heterogeneity index at conversion α_1 is given by:

$$\frac{\bar{y}_{w\alpha_1}}{\bar{y}_{n\alpha_1}} = \frac{2}{(r\alpha_1)^2} (e^{r\alpha_1} - 1) (1 - e^{-r\alpha_1}) . \quad (14)$$

The heterogeneity index is seen to depend only on the value of the product $r\alpha_1$ and to be independent of the magnitude of the average degree of polymerization. This implies (cf. Equation (12)) that the heterogeneity index depends only on the fractional depletion of modifier, and not on the amount (or type) of modifier used.

By means of Equations (12) and (14) it can be shown that at the point of 50% depletion of modifier the heterogeneity index rises only to 2.08. With further depletion the heterogeneity index increases somewhat more rapidly, reaching the value 3.06 when 90% depletion has taken place.

The effect of modifier depletion on the cumulative primary distribution is illustrated further by the following calculations. A value of 0.999 is taken for p_0 corresponding to a number average degree of polymerization \bar{y}_n of 1000 units for the polymer formed initially. The distributions (W_y) for the polymer formed up to 50 and 90% depletion of modifier were calculated by means of Equation (10) with p_1 equal to 0.9995 and 0.9999, respectively. These distributions are shown in Fig. 1. For comparison the increment distributions (Equation (7)) for the same number average primary molecular size are shown ($p = 0.99928$ and 0.99961). The latter curves represent the distributions that would have resulted from 50 and 90% depletion of modifier, had the modifier and monomer been used up at the same relative rate. It is seen that up to at least 50% depletion of modifier the *form* of the distribution is distorted only slightly. Further distortion is found at 90% depletion but

even for this extent of modifier disappearance the increase of heterogeneity in the size distribution of the primary molecules is not marked.*

In the foregoing discussion, no mention is made of the possibility of branching reactions, such as may occur as a result of chain transfer with a hydrogen atom on the body of another molecule (2, 5, 26). Although such branching

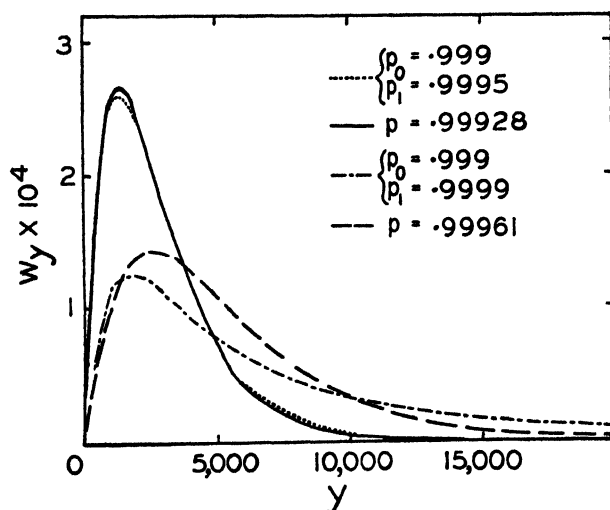


FIG. 1. Typical cumulative distributions for 50% and 90% depletion of modifier.

reactions may distort the primary molecular size distribution somewhat, they do not alter the 1 : 1 ratio of modifier fragments to polymer molecules, nor do they interfere in any way in the application of the statistical theory of gelation (35).

Gel Formation

The theoretical aspects of cross-linking have been examined statistically by Flory (6, 7, 12) and Stockmayer (34, 35). As polymer molecules are bonded together, large structures are gradually built up, a process that eventually results in the formation of "infinite networks" pervading the entire volume. Such networks are insoluble in normal solvents for the polymer and constitute the gel fraction.

On the assumption that cross-linking is random and that intramolecular connections within the sol fraction may be neglected, Flory has derived equations that, when applied to specific initial distributions, relate the weight fraction of gel and other quantities of interest to the degree of cross-linking (12). The degree of cross-linking, designated by ρ is defined as the fraction of structural units (monomer) involved in cross-linkages. In obtaining the various relations Flory has employed a quantity ϕ , defined as the probability that a non-cross-linked structural unit selected at random is part of the sol fraction. The weight fractions of sol and gel are designated by W_s and W_g ,

* The measured heterogeneity of the actual molecular size distribution is generally found to exceed estimates made in this way, probably as a result of cross-linking during polymerization (13, 38). The primary distribution, by definition, is unaffected by such cross-linking reactions.

respectively. The statistical relations between ρ , W_s , ϕ_s , and the initial primary molecular size distribution, W_v , are given by:

$$\frac{W_s}{\phi_s} \doteq 1 - \rho (1 - W_s) \quad (15)$$

$$W_s = \sum_{v=1}^{\infty} W_v \left(\frac{W_s}{\phi_s} \right)^v. \quad (16)$$

For a given *form* of primary distribution an explicit relation exists between the weight fraction of gel, and the average number of cross-linked units per primary molecule $\rho \bar{y}_n$. Methods of calculating this relation for a polymer of homogeneous molecular weight and for the "increment" distribution [Equation (7)] have been given by Flory (12). The results are plotted in Fig. 2.

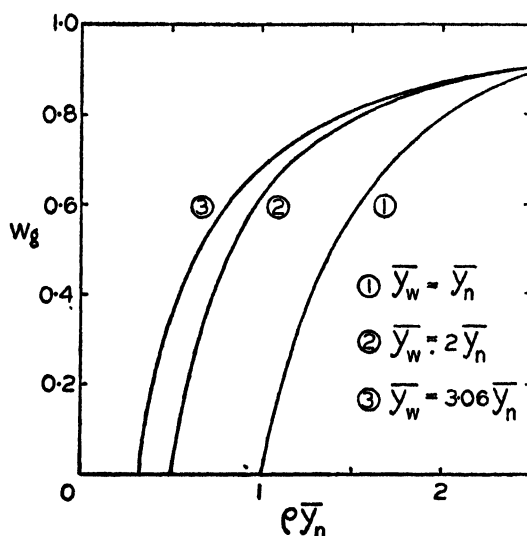


FIG. 2. Statistical relation between weight fraction of gel and average number of cross-linked units per primary molecule; for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

The relation for the cumulative distribution may be found by substituting Equation (10) in Equation (16) and evaluating the summations. The final result is:

$$W_s = \frac{1}{r \alpha_1} \left\{ \frac{(1 - p_1) p_1 \frac{W_s}{\phi_s}}{1 - p_1 \frac{W_s}{\phi_s}} - \frac{(1 - p_0) p_0 \frac{W_s}{\phi_s}}{1 - p_0 \frac{W_s}{\phi_s}} \right. \\ \left. + \frac{1}{\frac{W_s}{\phi_s}} \left[\ln \frac{1 - p_0 \frac{W_s}{\phi_s}}{1 - p_1 \frac{W_s}{\phi_s}} \right] + p_0 - p_1 \right\}$$

Calculations were made for the specific case of 90% modifier depletion, i.e.,

$$\frac{1 - p_0}{1 - p_1} = \frac{R_0}{R_1} = 10$$

$$r \alpha_1 = 2.303$$

$$y_w = 3.06 y_n .$$

Values of 0.999 and 0.9999 were used for p_0 and p_1 and the values of W_s for arbitrary values of $\frac{W_s}{\phi_s}$ deduced. Substitution of these values in Equation (15) yielded values of ρ from which the quantity $\rho \bar{y}_n$ was then obtained. Curve (3) of Fig. 2 shows the weight fraction of gel vs. $\rho \bar{y}_n$ for the distribution resulting from 90% depletion of modifier.

The course of gelation is seen to be similar for the three distributions considered. The gel fraction appears when ρ exceeds $\frac{1}{y_w}$ (35) and then increases rapidly with further cross-linking, approaching unity asymptotically.

The constitution of the gel fraction itself will now be considered. The degree of cross-linking of the gel fraction, ρ'' , is related (12) to ρ , the degree of cross-linking of the aggregate of sol and gel, by the equation:

$$\rho'' = \rho (2 - W_g) .$$

The number average degree of polymerization \bar{y}_n' of the primary molecules in the sol fraction is given by:

$$\bar{y}_n' = \frac{W_s}{\sum_{y=1}^{\infty} \frac{W_y}{y} \left(\frac{W_s}{\theta_s} \right)^y} . \quad (17)$$

The corresponding number average degree of polymerization \bar{y}_n'' of the primary molecules in the gel fraction can be obtained by difference. The total number of primary molecules per structural unit is $\frac{1}{\bar{y}_n}$. If a weight fraction of gel, W_g , is present, the number of primary molecules in the gel is $\frac{W_g}{\bar{y}_n''}$ and that in the sol $\frac{1 - W_g}{\bar{y}_n'}$. The value of \bar{y}_n'' is determined by:

$$\frac{W_g}{\bar{y}_n''} = \frac{1}{\bar{y}_n} - \frac{1 - W_g}{\bar{y}_n'}$$

Consequently if the primary distribution is known and the gel fraction has been measured, the constitution of the gel with respect to degree of cross-linking and primary molecular size may be deduced.

Of particular interest from the viewpoint of elasticity theory is the degree of *cyclic* cross-linking, or the number of "effective" chains per structural unit. It will be recalled from the considerations leading to Equation (3) that if all

of the molecules have been linked to the network the number of "effective" chains per structural unit is $\rho - \frac{2}{\bar{y}_n}$. If, however, the degree of cross-linking is sufficiently low that an appreciable sol fraction results, attention must be confined to the gel fraction, since soluble molecules make no permanent contribution to the retractive force. Consequently the number of "effective" chains per structural unit is $\rho'' - \frac{2}{\bar{y}_n''}$ and the number of "effective" chains per primary molecule is $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$.

The function $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ may be calculated for various forms of the initial primary distribution. This calculation has been made for the three cases considered above; viz., the homogeneous, increment, and cumulative distributions. The summation involved in Equation (17) and the remaining calculations were made in a manner exactly analogous to that employed in deducing the relation between W_g and $\rho \bar{y}_n$.

In Fig. 3 the function $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ is plotted against $\rho \bar{y}_n$ for the three distributions considered (The cumulative distribution employed corresponds

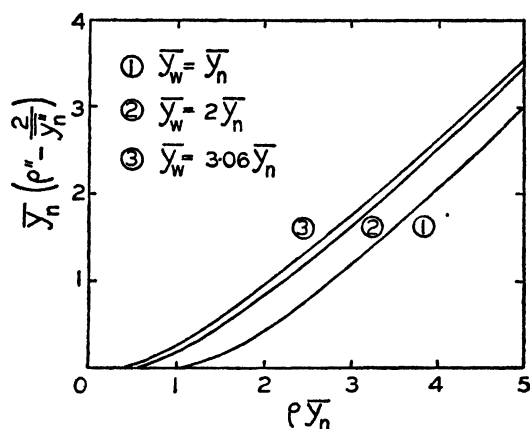


FIG. 3. Statistical relation between the number of effective chains and the average number of cross-linked units per primary molecule for (1) homogeneous polymer, (2) increment, and (3) cumulative distributions.

to 90% modifier depletion). It is seen that after gelation begins, "cyclic" cross-linkages form at an accelerating rate with further cross-linking. In general the relation of the various distributions to one another is similar to that found for the gel fraction (Fig. 2).

This relation is demonstrated further in Fig. 4, where $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ is plotted against the corresponding sol fraction. Over a considerable range of solubility the measured gel fraction is associated with about the same average

number of "effective" chains per primary molecule for all of the distributions considered.

The statistical relations discussed above will be employed in a subsequent paper dealing with the formation and properties of butadiene-styrene copolymer networks.

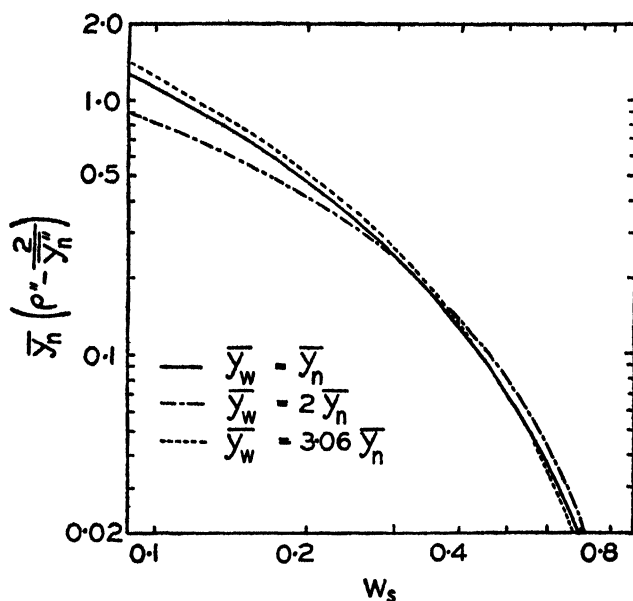


FIG. 4. Statistical relation between the number of effective chains per primary molecule and the weight fraction of sol for homogeneous polymer, increment, and cumulative distributions (log-log plot).

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

II. NETWORK FORMATION¹

BY J. BARDWELL² AND C. A. WINKLER

Abstract

Addition of potassium persulphate to a latex leads to cross-linking with typical diene polymers but has little effect on polystyrene. The rate of cross-linking is directly proportional to the persulphate concentration. The activation energy is 26,900 cal. The rate depends on latex particle size and is affected by the presence of other reagents. The course of gelation supports the predictions of the statistical theory of random cross-linking.

Introduction

The development of three-dimensional network structures when cross-linkages are introduced between polymer molecules has been subjected to detailed statistical analysis (6, 16). On the other hand experimental study of the cross-linking processes that occur in conventional vulcanizations is hampered by the reaction conditions employed and by the variety of side reactions encountered. The theory of network formation is therefore at a more advanced stage of development than experiment.

A simpler method of cross-linking polymer molecules has been developed in this laboratory. The addition of potassium persulphate to an emulsion of polymer (e.g., a latex) leads to the formation of insoluble three-dimensional structures.

Experimental

Cross-linking Reaction

The polymer used in most of the investigations described below was the well known copolymer of butadiene and styrene (GR-S), in the form of a monomer-free latex prepared by Polymer Corporation, Sarnia. The modifier used was commercial dodecyl mercaptan and the conversion was 70%.

To promote cross-linking, a solution of potassium persulphate buffered with an equimolar mixture of sodium carbonate and sodium bicarbonate was added to the latex, the final mixture having the following composition:

Polymer (GR-S)	5.0%
Potassium persulphate	2.5%
Buffer (sodium carbonate – sodium bicarbonate)	1.5%

After thorough mixing, aliquots of 25 cc. were transferred to one-ounce bottles. Nitrogen was bubbled through the reaction mixture for 30 secs.,

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after which the bottle was capped tightly and immersed in a water bath at $50.0 \pm 0.5^\circ \text{C}$. After suitable intervals the reaction was stopped by coagulating the polymer in rapidly stirring butanol containing 0.05% phenyl- β -naphthylamine antioxidant (P.B.N.A.). The coagulum was washed with butanol, 2% P.B.N.A. was added, and the polymer was dried for 12 hr. at 80°C . in a vacuum oven.

Solubility and Swelling

Weighed fragments of the dried polymer were placed in small screen cages and extracted for 48 hr. in toluene containing 0.05% P.B.N.A. The cage containing the swollen gel was then placed on a pad of filter paper in a small closed container and allowed to drain for five minutes. After its weight was determined, the swollen gel was dried to constant weight and the gel fraction and "swelling volume" calculated, using the values of 0.93 and 0.86 for the densities of GR-S and toluene respectively. The solubility was corrected for the small amount of nonpolymer components extractable in ethanol-toluene azeotrope containing 10% water (11).

Values of gel fraction and swelling volume determined in this way depend somewhat on the extent to which the polymer is dried. Unless the coagulum is thoroughly dried, colloidal dispersion of "microgel" may interfere, leading to low values for the gel fraction (15). This effect is illustrated in Fig. 1, which shows that the measured gel fraction increases as the time of drying is increased,

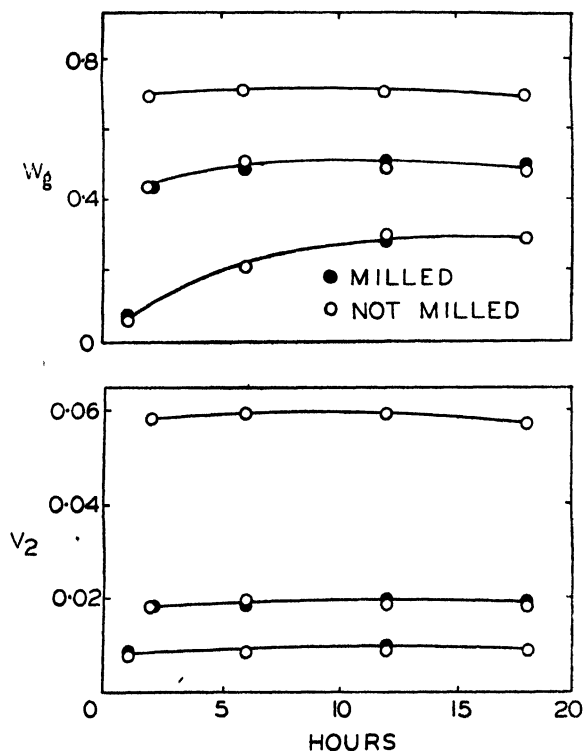


FIG. 1. Effect of heating at 80°C . in a vacuum oven, on the measured gel fraction, W_g , and reciprocal swelling volume, v_2 .

particularly when the insoluble fraction is small. The effect of drying has been thoroughly investigated by Medalia and Kolthoff (15), who have shown that heating for 12 hr. at 80° C. in a vacuum oven is effective in minimizing colloidal dispersion of "microgel" with GR-S polymers. The results shown in Fig. 1 support this conclusion. Mechanical mixing (milling) of the coagulum prior to heating does not appear to have any significant effect on the values obtained.

Thorough drying of the polymer has the additional advantage that the values obtained are insensitive to variations in the time and temperature of extraction. The results shown in Fig. 2 indicate that the rate of extraction does not depend

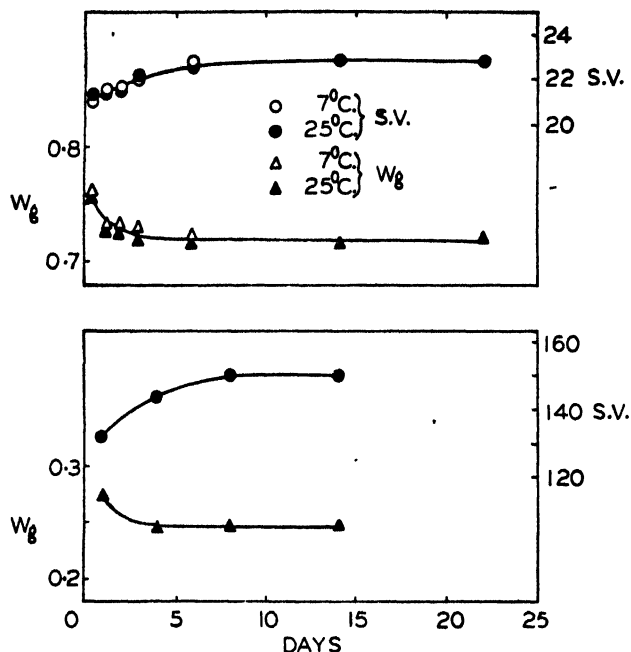


FIG. 2. Effect of prolonged extraction on the measured gel fraction, W_g , and swelling volume, S.V.

markedly on temperature between 7 and 25° C., and that removal of soluble polymer is virtually complete after 48 hr. The slow increase of swelling during the next few days is believed to result from oxidative breakdown (7, p. 179); the value after 48 hr. may then be accepted as approximating the equilibrium swelling volume.

Baker has shown that several solvents give the same value of gel fraction with GR-S polymers (1). This conclusion was verified and extended by extracting portions of a partially soluble polymer with toluene, benzene, xylene, nitrobenzene; chlorobenzene, chloroform, carbon tetrachloride, ethyl ether, and methyl amyl ketone. Despite the diverse chemical nature of the solvents employed, the measured gel fraction showed a variation of less than 2%.

The foregoing results indicate that the method used for determining solubility and swelling is suitable for characterizing cross-linked polymers.

Results and Discussion

When potassium persulphate is added to GR-S latex, the polymer undergoes a progressive loss of solubility. The swelling volume of the gel also decreases. Typical results are shown in Fig. 3, in which the gel fraction (W_g) and recip-

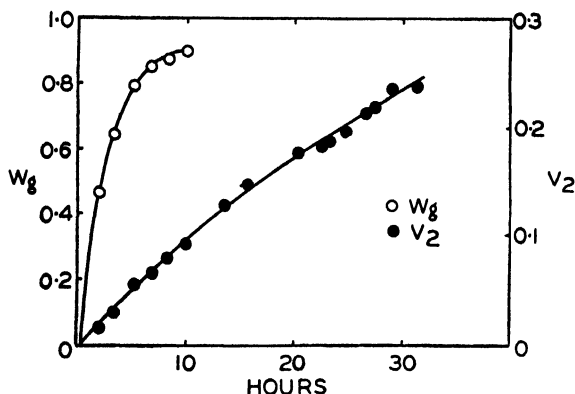


FIG. 3. Rate of increase of gel fraction and reciprocal swelling volume.

rocal swelling volume (v_2) are plotted vs. time of reaction. Further evidence of the cross-linking reaction is found in the increasing hardness of the dried coagulum. Several other features of this reaction were investigated, as follows.

Viscosity of Soluble Polymer

The viscosity of the solution remaining after removal of the gel fraction was measured in an Ubbelohde viscometer at 25° C., and the intrinsic viscosity $[\eta]$ determined by extrapolating to zero concentration. The results given in Table I show that the molecular weight of the sol fraction decreases as gelation proceeds. This result is in agreement with the statistical theory of random cross-linking (6).

TABLE I
INTRINSIC VISCOSITY OF SOLUBLE FRACTION

Gel fraction	$[\eta]$
0	2.09
0.29	1.60
0.44	1.31
0.70	0.72
0.81	0.25

Decomposition of Persulphate

Green and Masson have shown that the decomposition of persulphuric acid or its salts in aqueous solution is generally first order, the rate constant depending slightly on the composition of the reaction medium (10). The rate

constant for persulphate decomposition at 50° C. in latex buffered at a pH of about 9 was determined from measurements of residual persulphate by the method of Kolthoff *et al.* (12). Control experiments showed that the presence of a small amount of latex did not interfere with the analysis and did not greatly affect the rate of persulphate decomposition. The results shown in Fig. 4 yield a first order velocity constant, k , of 0.0084 hr.⁻¹; i.e., the half-life of the persulphate ion at 50° C. is about 83 hr., a satisfactorily long period.

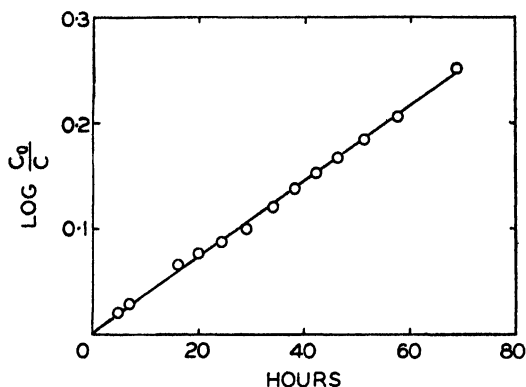


FIG. 4. First order decomposition of potassium persulphate in buffered latex at 50° C.

The Energy of Activation

The rate of cross-linking was determined at four temperatures ranging from 30 to 76° C., and expressed in arbitrary units based on the time required to produce a given gel fraction. The data shown in Table II yield an energy of activation of about 26,900 cal., a value quite close to that of 26,000 cal. obtained by Eager and Winkler for the decomposition of potassium persulphate in aqueous 80% acetic acid (5).

TABLE II
EFFECT OF TEMPERATURE ON RATE OF CROSS-LINKING

Temperature, °C.	Rate of cross-linking (arbitrary units)
30.1	1
50.0	18
60.0	65
76.0	370

Unbuffered System

When no buffer is included, the course of the reaction is complicated by increasing acidity which results from the decomposition of persulphate. The most obvious result of the fall of pH is agglomeration of the latex particles, revealed by loss of Tyndall effect and eventually by coagulation.

The pH of the reaction mixture was measured with a glass electrode, and particle size of the latex by the method of light scattering (2, 4). For the latter measurements the reaction mixture was diluted to suitable concentrations with dilute (0.06%) soap solution and the turbidity measured with a Beckman spectrophotometer. Particle diameters were calculated from the turbidity-concentration ratio at infinite dilution (2).

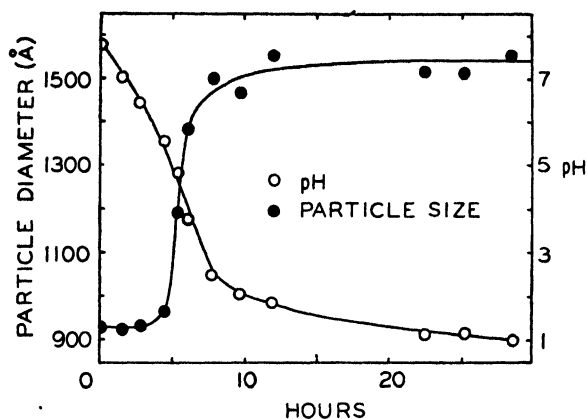


FIG. 5. Change of pH and particle size with progress of reaction (unbuffered).

In Fig. 5, pH and particle diameter are plotted against time of reaction. It is interesting to note that no appreciable agglomeration of the latex particles occurs until the pH falls to about 6. Average particle diameter then rises sharply from about 900 Å to about 1500 Å after which little further change occurs. In the latter region however, the emulsion appears to be metastable; a coagulum separates when the mixture is agitated.

When the reaction mixture is adequately buffered, practically no agglomeration occurs for several days. The results given in Table III show that changes of pH and particle size are very slow when the usual amount of buffer is included.

TABLE III

CHANGE OF pH AND PARTICLE SIZE IN BUFFERED REACTION MIXTURE AT 50.0° C.

<i>Reaction mixture</i>		
Polymer (GR-S)	5.0%	
Potassium persulphate	2.5%	
Buffer (sodium carbonate - sodium bicarbonate)	1.5%	
Reaction time, hr.	pH	Particle diameter, Å
0	9.7	930
12.2	9.5	950
24.0	9.2	975
48.1	8.4	1030

Factors affecting the Rate of Cross-linking

At a given concentration of polymer and potassium persulphate, the rate of cross-linking is affected by the presence of other materials. In Table IV are shown the effects of various added reagents on the rate of insolubilization.

TABLE IV
EFFECT OF VARIOUS REAGENTS ON THE RATE OF INSOLUBILIZATION AT 50° C.

<i>Reaction mixture</i>		
Polymer (GR-S)	13%	
Potassium persulphate	1.5%	
Buffer (sodium carbonate – sodium bicarbonate)	0.9%	
Reaction time—16 hr.		
Reagent added	Gel fraction	Reciprocal swelling volume
None	0.836	0.0636
0.1% silver nitrate	0.880	0.0752
0.8% <i>n</i> -dodecyl mercaptan; bottle flushed with nitrogen	0.919	0.0980
0.8% <i>n</i> -dodecyl mercaptan; bottle flushed with oxygen	0.787	0.0566
8% <i>n</i> -dodecyl mercaptan; bottle flushed with nitrogen	0.785	0.0406
16% toluene	0.457	0.0108
0.08% phenyl- β -naphthylamine	0.393	0.0119
0.8% hydroquinone	0.145	0.0058

It is seen that small amounts of silver ion and of *n*-dodecyl mercaptan have an accelerating effect on the cross-linking reaction. The action of silver ion as a "catalyst" for oxidations involving persulphate (8, p. 1118) and the role of traces of mercaptans as "promoters" in the polymerization of butadiene (13) are well known. Similarly the use of phenyl- β -naphthylamine as an antioxidant and of hydroquinone as a "shortstop" in polymerizations is widespread, and their retarding effect on the cross-linking reaction is not unexpected. The retardation caused by relatively large amounts of *n*-dodecyl mercaptan and of toluene may be due to chain transfer activity or merely to dilution of the polymer. The apparent retarding effect of traces of *n*-dodecyl mercaptan *in the presence of oxygen* may be due to a competing scission reaction. Some evidence for such a reaction with soluble polymer has been found by Kolthoff and Stenberg (14). When no mercaptan was added, however, the rate of insolubilization was found to be unaffected by the presence of oxygen. The addition of soap to the latex was likewise found to be without effect.

Some evidence was found to show that the rate of insolubilization depended on the particle size of the latex. When the reaction mixture was cooled and subjected to prolonged centrifuging, some of the larger particles collected at the surface. Comparison with the remaining latex indicated that the polymer within these larger particles had become cross-linked at a rate that was about 20% smaller than the rate of cross-linking of the remainder. This result

suggests that the *initial* activation of the polymer takes place only at the polymer-water interface.

At a given concentration of polymer the rate of cross-linking was found to increase as the initial concentration of persulphate was increased. The effect of persulphate concentration was investigated quantitatively by interpreting the resulting gel fraction through the statistical theory of gelation (3, 6). For this purpose the form of the primary molecular size distribution of the polymer used was assumed to be given to an adequate approximation by the theoretical cumulative distribution (3, Equation 10), corresponding to 90% modifier depletion. The theoretical course of gelation for this distribution has been calculated (3, Curve 3 of Fig. 2). By means of this relation the rates of cross-linking for various initial concentrations of potassium persulphate were calculated from the observed increase of gel fraction. The

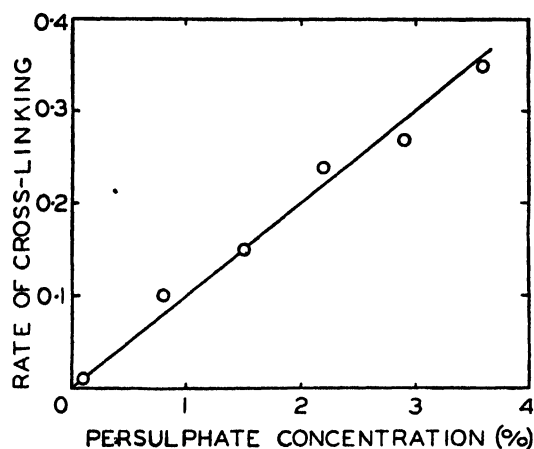


FIG. 6. Effect of initial persulphate concentration on the rate of cross-linking.

results shown in Fig. 6 demonstrate that the rate of cross-linking is directly proportional to the concentration of persulphate, i.e.,

$$\frac{d\rho}{dt} = k_x c, \quad (1)$$

ρ = fraction of structural units involved in cross-linkages,

c = concentration of persulphate,

k_x = cross-linking velocity "constant"

for the reaction conditions employed (polymer concentration, latex particle size, etc.)

Since the decomposition of persulphate is first order (Fig. 4) the concentration at time t is given by

$$c = c_0 e^{-kt}$$

Substituting for c in Equation (1) and integrating

$$\rho = \rho_0 + k_x c_0 \left(\frac{1 - e^{-kt}}{k} \right). \quad (2)$$

ρ_0 and c_0 are the values of ρ and c initially.

On this basis it is to be expected that, as the time of reaction increases, the degree of cross-linking of the polymer will be linear with $\frac{1 - e^{-kt}}{k}$, or to a first approximation with t since k is small at 50° C.

The results shown in Fig. 3 provide excellent confirmation of this prediction. The average number of cross-linked units per primary molecule ($\rho\bar{y}_n$) was

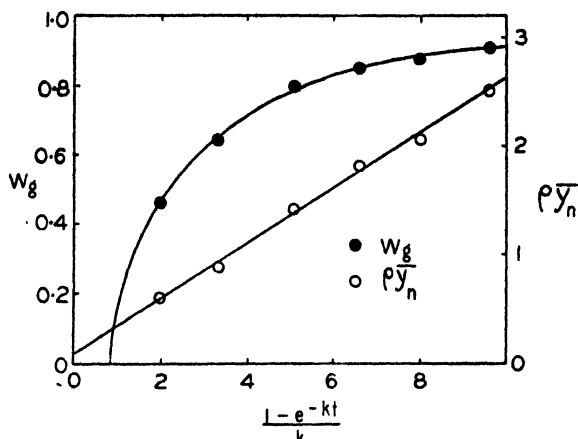


FIG. 7. Weight fraction of gel and average number of cross-linked units per primary molecule, vs. $\frac{1 - e^{-kt}}{k}$ (Equation 2).

calculated from the observed gel fraction and is shown in Fig. 7 as a function of $\frac{1 - e^{-kt}}{k}$ computed from the reaction time with $k = 0.0084 \text{ hr.}^{-1}$: The relation is linear and can be expressed by the equation:

$$\rho\bar{y}_n = 0.09 + 0.254 \left(\frac{1 - e^{-kt}}{k} \right). \quad (3)$$

A plot of $\rho\bar{y}_n$ vs. time is nearly as satisfactory since over this interval the concentration of persulphate changes by less than 10%. The linearity of these plots shows that the course of gelation predicted by statistical theory is in harmony with the experimental results for the cross-linking reaction under investigation.

Extrapolation of the line in Fig. 7 to zero time permits estimation of the degree of cross-linking of the initial (soluble) polymer. Moreover, a simple method now becomes available for calculating the degree of cross-linking of the virtually insoluble polymers resulting from longer reaction periods. The determination of these quantities by direct experiment is usually difficult.

For the polymer involved here, the value of \bar{y}_n , the average primary chain length, may be estimated from modifier consumption to be of the order of 800 units. Comparing Equations (2) and (3), the deduced value of $k_x c_0$ is then about 3×10^{-4} for the experimental conditions employed.

Scission

Taylor and Tobolsky have suggested that cross-linking and scission reactions generally compete with each other in polymeric media when free radicals

are present (17). Although the insolubilization of the polymer shows that cross-linking is the predominant reaction taking place when potassium persulphate is added to GR-S latex, the possibility of a simultaneous degradative process should not be ignored.

Direct evidence on the rate of scission reactions, if present, is difficult to obtain with diene polymers because of the gelation caused by cross-linking. With vinyl polymers however, cross-linking does not seem to occur to any appreciable extent, and the rate of scission may be found from viscosity measurements. Accordingly, the effect of potassium persulphate on polystyrene latex was investigated.

For this purpose a polystyrene latex of 88% conversion was prepared by the bottle polymerization method (13). Residual styrene was removed by vacuum distillation at about 40° C. When treated with potassium persulphate, the polystyrene remained completely soluble but the viscosity molecular weight decreased slightly. Over a period of 41 hr. the intrinsic viscosity fell from 2.5 to 2.3.

By analogy with the quantitative treatment of cross-linking, the "scission rate constant" k_s may be defined by the equation:

$$\frac{d\left(\frac{1}{\bar{y}_n}\right)}{dt} = k_s c,$$

\bar{y}_n = number average degree of polymerization,

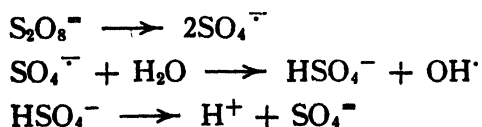
c = concentration of persulphate.

Values of \bar{y}_n were estimated from the intrinsic viscosity by means of the equation obtained by Goldberg, Hohenstein, and Mark (9). Calculation showed that for the same reaction conditions the scission rate constant, k_s , for polystyrene was less than 1% of the apparent cross-linking velocity constant, k_x , for GR-S. If the rate of scission with GR-S is of the same order of magnitude as with polystyrene it is evident that cross-linking is by far the dominant reaction at the temperature used.

Conclusions

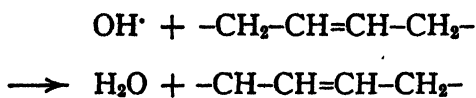
From an experimental viewpoint the use of potassium persulphate provides an attractively simple means of cross-linking diene polymer molecules. The reaction proceeds at a steady and easily controlled rate without seriously depleting the reaction source or contaminating the polymer with foreign materials.

A mechanism for the cross-linking may be inferred by analogy with the role of persulphates in the initiation of polymerizations. It appears likely that the first step in the process is thermal decomposition of the persulphate ion, viz.,

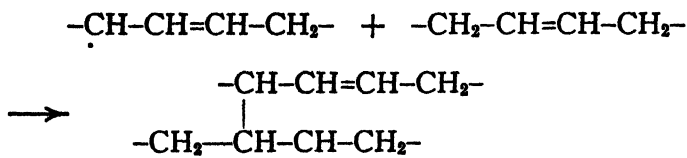


A plausible mechanism for the subsequent cross-linking would seem to be:

(1) Dehydrogenation at the α -methylene carbon of a polymerized butadiene unit:



(2) Addition of the free radical so formed to an unsaturated carbon of another polymerized butadiene unit:



Cross-linking may also occur when two such polymeric radicals combine.

Although the *initial* activation of the polymer probably occurs only at the polymer-water interface, the rapid loss of solubility suggests that the subsequent cross-linking takes place in a fairly uniform manner throughout the whole latex particle. The tendency for random cross-linking is favored by the minute dimensions of latex particles and the possibility of frequent chain transfer of the active center prior to the actual inter-linking step.

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THE FORMATION AND PROPERTIES OF THREE-DIMENSIONAL POLYMERS

III. THE EFFECT OF NETWORK STRUCTURE ON ELASTIC PROPERTIES¹

J. BARDWELL² AND C. A. WINKLER

Abstract

The tension exerted by stretched rubber at a given temperature and elongation is determined by the initial molecular weight and the concentration of cross-linkages. With the copolymer of butadiene and styrene (GR-S), the effect of molecular weight on elastic properties is identical with that found by Flory for butyl rubber and arises from the inactivity of terminal chains. When the molecular weight is fixed, the retractive force is approximately linear with the degree of cross-linking, in agreement with the statistical mechanics of rubber elasticity.

Introduction

In a previous paper of this series theoretical treatments of the elastic behavior of three-dimensional polymers were reviewed (1). It is the purpose of the present paper to compare the theoretical predictions with the observed behavior of networks formed from the copolymer of butadiene and styrene (GR-S).

Experimental

Preparation of Polymers

The GR-S polymers were prepared in emulsion by the well known bottle polymerization method (21, 26). The following recipe was employed.

Water	180 parts
Butadiene	75 "
Styrene	25 "
Soap	5 "
Potassium persulphate (Merck's reagent grade)	0.3 "
Tertiary dodecyl mercaptan (Sharples 3-B)	Variable

By varying the amount of mercaptan used a wide range of molecular weight was obtained. The number average degree of polymerization, \bar{y}_n , and the heterogeneity index, $\frac{\bar{y}_w}{\bar{y}_n}$, of the primary molecules were calculated by means of equations given previously (1, Equations 13 and 14). The "regulating index" of tertiary dodecyl mercaptan is 3.16 (26). In computing chain lengths due allowance was made for compositional changes during polymerization (24). Relevant characteristics of the polymers are given in Table I.

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² Holder of a National Research Council Fellowship. Present address: Physical Chemistry Laboratory, Oxford, England.

TABLE I

DEGREE OF POLYMERIZATION AND HETEROGENEITY INDEX OF MODIFIED GR-S POLYMERS

Polymer No.	Mercaptan charged (moles per mole of initial monomer), R_0	Conversion α	Number' average degree of polymerization \bar{y}_n	Heterogeneity index $\frac{\bar{y}_w}{\bar{y}_n}$
I	0.44	0.304	11600	2.16
II	1.42	0.232	3150	2.09
III	2.95	0.465	2080	2.38
IV	4.47	0.107	870	2.02
V	4.47	0.275	1100	2.13
VI	4.47	0.356	1220	2.22
VII	7.37	0.171	575	2.05
VIII	14.2	0.136	275	2.03
IX	58.9	0.515	110	2.52

Cross-linking Reaction

After the addition of a small amount of hydroquinone to prevent further polymerization, residual monomer was removed from the emulsion by vacuum distillation at about 40° C. A buffered solution of potassium persulphate was then added to promote cross-linking (2).

To compare this cross-linking reaction with more conventional vulcanizations, one of the polymers (VI) was mixed with compounding ingredients and cured at 140° C. The curing ingredients were added as a colloidal dispersion to the latex, which was then coagulated in butanol. The composition of the coagulum was approximately as follows:

Polymer	100 parts
Sulphur	2 "
Benzthiazyl disulphide	2 "
Phenyl- β -naphthylamine	2 "
Zinc oxide	1 "

After a short period of milling at room temperature to obtain thorough mixing, portions of the coagulum were cured at 140° C.

Solubility and Swelling

The gel fraction and swelling volume of the cross-linked polymers were determined by the static extraction method (2).

Modulus

Stress-strain curves were determined for several GR-S pure gum vulcanizates by means of a standard testing machine. The rate of extension was 20 in. per min. In addition to the "dynamic" modulus obtained in this way, the "static" modulus was estimated by subtracting the stress-relaxation that took place when a test specimen was held at a relative elongation of 300% for 24 hr.

Results and Discussion

The Relation of Swelling to Modulus

In a previous paper (1) it was pointed out that several theoretical treatments of the phenomenon of rubberlike elasticity lead to an "equation of state" of the form:

$$\tau = \frac{\nu}{V} RT \left(\frac{l}{l_0} - \frac{l_0^2}{l^2} \right) \quad (1)$$

τ = tension (force per unit area of initial cross section),

R = gas constant,

T = absolute temperature,

l = stretched length,

l_0 = unstretched length.

Several authors (11, 30, 31) have interpreted ν as the number of "chains" in volume V , but here it is convenient to consider the ratio $\frac{\nu}{V}$ as the "network activity", i.e., as an *experimental* quantity defined by Equation (1). Here, it is the dependence of $\frac{\nu}{V}$ on network structure that is of main concern.

Consideration of the phenomenon of swelling as a three-dimensional stretching (12) results in a relation between equilibrium swelling volume and "network activity" $\frac{\nu}{V}$:

$$\frac{\nu}{V} = \frac{\ln(1 - v_2) + v_2 + \mu_0 v_2^2}{-V_1 v_2^{\frac{1}{2}}} \quad (2)$$

v_2 = reciprocal of the equilibrium swelling volume,

μ_0 = solvent-polymer interaction coefficient (7, 18),

V_1 = molar volume of solvent.

By expanding the term $\ln(1 - v_2)$ and combining the resulting expression with Equation (1), it is found that the "modulus" (tension at a given elongation) of the unswollen rubber is predicted to be approximately inversely proportional to the 5/3 power of the equilibrium swelling volume.

Measurements of modulus and swelling with GR-S pure gum vulcanizates amply confirm this relation. Fig. 1 consists of a log-log plot of the "dynamic" and "static" moduli at 300% elongation (τ_{300}) vs. the equilibrium swelling volume in toluene ($S.V.$). Although both dynamic and static moduli show good correlation with the swelling volume, better agreement with theory is found for the static modulus. This result is not surprising, since swelling represents an equilibrium type of deformation.

The equation of the line in Fig. 1 for the static modulus is

$$\log \tau_{300} = 3.67 - 1.67 \log S.V.$$

The theoretical slope of $(-5/3)$ is found and the Flory-Rehner treatment of swelling thereby substantiated (12). By comparing the above results with Equations (1) and (2) the value of μ_0 for GR-S in toluene is found to be 0.18.

Small variations of styrene content of the polymer do not appear to alter this value significantly (Fig. 1).

The observed correlation between modulus and equilibrium swelling volume agrees with results obtained with butyl rubber (6, 8), and provides further

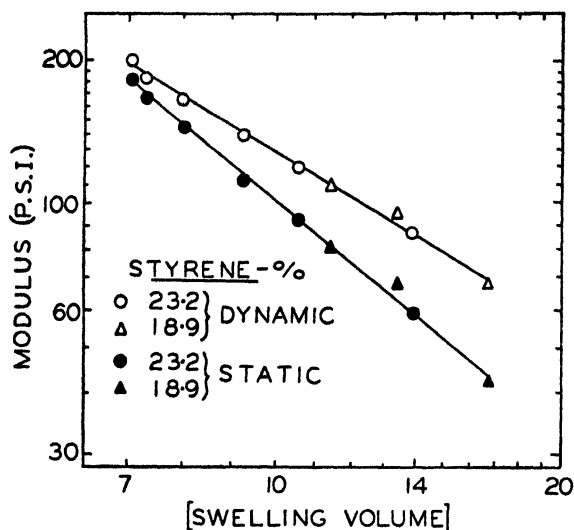


FIG. 1. Modulus at 300% elongation vs. swelling volume (log-log plot).

evidence that the elastic reaction in both deformation processes is governed by the same structural factors. The "network activity" may therefore be estimated from either measurement.

The Coefficient μ_0

Since the thermodynamic properties of polymer solutions and gels are still under active discussion (3, 15), it seems worthwhile to consider briefly values of the coefficient μ_0 as estimated from the swelling-modulus correlation. Table II shows the measured values of the equilibrium swelling volume of a GR-S gel in various organic solvents, together with values of μ_0 calculated by means of Equation (2).

TABLE II
SWELLING CHARACTERISTICS OF GR-S IN VARIOUS LIQUIDS

Liquid	Equilibrium swelling volume	μ_0	Cohesive energy density, E_1 , cal./cc.
Ethyl ether	9.3	0.47	58
Methyl amyl ketone	11.3	0.40	61
Carbon tetrachloride	23.1	0.21	73
Xylene	22.4	0.14	77
Toluene	23.0	0.18	80
Benzene	22.0	0.26	84
Chloroform	25.9	0.20	86
Chlorobenzene	22.5	0.20	91
Nitrobenzene	9.3	0.47	99

In theory (7, 18) the quantity μ_θ is related to the heat of mixing of solvent and polymer by the equation

$$\mu_\theta = \frac{1}{Z} + \frac{\Delta\bar{H}_1}{RT v_2^2}, \quad (3)$$

Z = co-ordination number of the lattice model (7, 18),

$\Delta\bar{H}_1$ = partial molal heat of mixing,

v_2 = reciprocal swelling volume.

An approximate estimate of the partial molal heat of mixing may be made by means of the Scatchard expression (27)

$$\Delta\bar{H}_1 = V_1 v_2^2 (\sqrt{E_1} - \sqrt{E_2})^2 \quad (3')$$

E_1 and E_2 are the cohesive energy densities of solvent and polymer respectively.

Equations (3) and (3') suggest that μ_θ should pass through a minimum when $E_1 = E_2$. Cohesive energy densities for several liquids have been estimated by Gee (14, p. 183) and by Scott *et al.* (28) from heats of evaporation and are included in Table II. There appears to be a minimum in the value of μ_θ when E_1 is about 77 but chloroform and chlorobenzene are somewhat out of line, possibly because of their polar nature.

In comparing values of μ_θ estimated from the swelling-modulus correlation with those obtained by other methods, it is to be noted that the value of 0.26 for GR-S in benzene is less than the value of 0.36 found by French and Ewart from measurements of the osmotic pressure of dilute solutions of GR-S in benzene (13). A similar observation with butyl rubber (8) has been attributed to failure of the elementary statistical theory in the region of dilute solutions (7). If the lowest value of μ_θ (0.14 for xylene) is taken to correspond to zero heat of mixing, the co-ordination number Z appears to have an experimental value of about seven.

Swelling and Network Structure

In considering the effect of network structure on equilibrium swelling volume it is convenient to interpret the measured swelling in terms of the retractive force that the network exerts against the swelling pressure of the solvent. The "network activity", $\frac{\nu}{V}$, which appears in Equations (1) and (2) will be employed for this purpose.

The network structure, on the other hand, is determined by the concentration of cross-linkages and the molecular weight distribution prior to cross-linking (1, 6). If all the molecules are bound to the network the theoretical dependence of network activity, $\frac{\nu}{V}$, on these structural factors is given by:

$$\frac{\nu}{V} = g \frac{d}{M_0} \left(\rho - \frac{2}{\bar{y}_n} \right), \quad (4)$$

d = density of polymer,

M_0 = molecular weight of the structural unit (monomer),

ρ = fraction of structural units involved in cross-linkages,

\bar{y}_n = number average degree of polymerization prior to cross-linking,

g = a proportionality "constant" which has a theoretical value of unity in the Wall-Treloar-Flory-Rehner treatments of the elasticity problem (11, 30, 31). In the theory of Kuhn (22, 23), g has the value $7/3$ and in that of James and Guth (20) about $1/2$.

Equation (4), which presents an explicit connection between the "modulus" of vulcanized rubber and its network structure, has hitherto received only partial experimental verification. Flory (6, 8) has shown that the elastic properties of butyl vulcanizates of a fixed degree of cure (ρ constant) depend on primary molecular weight as indicated in Equation (4). The predicted effect of cross-linking has however received little direct support, and several alternative analyses of the phenomenon of elasticity have recently been proposed (17, 19, 25).

The determination of the primary molecular weight as required for experimental testing of Equation (4) presents no great difficulty if the polymerization kinetics are sufficiently understood. For example when a chain transfer agent (modifier) is present during chain growth, the primary molecular weight distribution may be calculated from modifier consumption (1).

The degree of cross-linking, ρ , is however a more elusive quantity and its determination requires closer examination of the process of network formation. In a previous paper (2) a method of cross-linking polymer molecules by the addition of potassium persulphate to a latex was described. It was shown that the conversion to gel in this process is in good agreement with the predictions of the statistical theory of random cross-linking. The measured gel fraction may therefore be interpreted as reflecting the presence of a definite concentration of cross-linkages in the polymer. Specifically, if the primary molecular weight distribution is known and the gel fraction has been measured, the degree of cross-linking of the polymer may be estimated with the assistance of suitable statistical relations (1, Fig. 2).

This principle was applied to the gels obtained by cross-linking the polymers listed in Table I. The degree of cross-linking, ρ , was calculated from the measured gel fraction, the heterogeneity index being employed for the necessary interpolations (1). The "network activity" $\frac{\nu}{V}$ was computed from the swelling volume by means of Equation (2) with the value of 0.18 for μ_0 .

Fig. 2 shows the effect of both primary chain length and degree of cross-linking on the "network activity" (modulus) of GR-S. The influence of primary molecular weight is particularly noteworthy. Polymers of low primary chain length are handicapped in the development of reversible elasticity since relatively large concentrations of cross-linkages are required for the formation of a network. Even after the "gel point" is reached, the

increase of modulus is less rapid than with polymers of high primary molecular weight, since a greater fraction of the additional cross-linkages are "wasted" in attaching new material to the network.

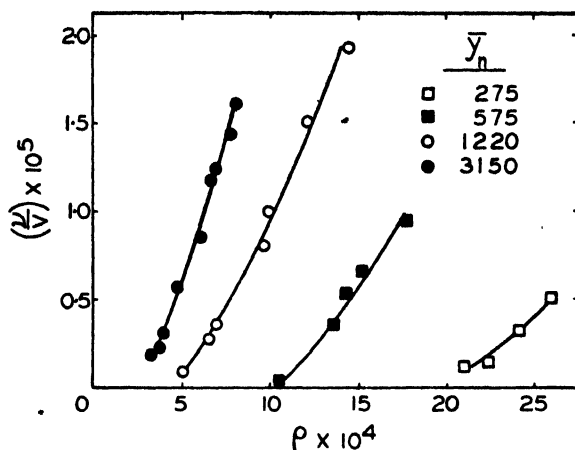


FIG. 2. Network activity vs. degree of cross-linking.

Before employing the results shown in Fig. 2 to test Equation (4), it should be noted that this Equation is intended only for completely insoluble polymers. When an appreciable fraction of extractable sol exists, only the structure of the gel is of interest. Equation (4) should then be modified to

$$\frac{\nu}{V} = g \frac{d}{M_0} \left(\rho'' - \frac{2}{\bar{y}_n''} \right), \quad (5)$$

ρ'' and \bar{y}_n'' are the values of ρ and \bar{y}_n in the gel.

To determine the "effective" degree of cross-linking $\left(\rho'' - \frac{2}{\bar{y}_n''} \right)$ it is necessary to consider the partition of cross-linkages and of primary molecules between sol and gel (9). Details of the required calculations and the results for various initial distributions were given previously (1). A plot of $\frac{\nu}{V}$ vs. $\rho'' - \frac{2}{\bar{y}_n''}$ then allows direct testing of the theoretical dependence of elastic modulus on network structure.

Fig. 3 shows that all the experimental results are in satisfactory agreement with Equation (5). The effect of molecular weight over a hundredfold range is therefore accounted for quantitatively by the postulate that terminal chains are inactive during deformation. The linearity of the resulting plot also verifies the proportionality between network activity and (effective) degree of cross-linking predicted by statistical mechanical treatments of rubber elasticity. The equation of the line in Fig. 3 is:

$$\frac{\nu}{V} = 0.039 \left(\rho'' - \frac{2}{\bar{y}_n''} \right).$$

Substituting $d = 0.93$

$M_0 = 59.2$

in Equation (5), the value of g is found to be 2.5, in good agreement with the value of $7/3$ predicted by Kuhn.

Fig. 3 includes results deduced from the swelling and solubility of GR-S pure gum vulcanizates at low degrees of cure. The above conclusions concerning the effect of network structure on elastic properties appear to be equally applicable to GR-S vulcanizates.

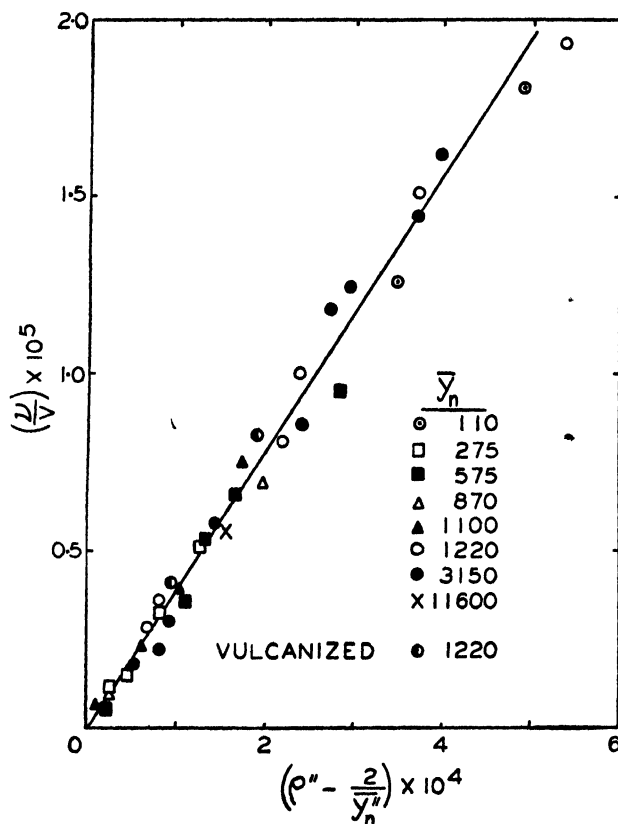


FIG. 3. Network activity vs. effective degree of cross-linking.

The effect of much higher concentrations of cross-linkages was investigated by extending the reaction period with one of the polymers (III). The degree of cross-linking of the resulting essentially insoluble polymers was calculated from the measured *rate* of insolubilization early in the reaction, due allowance being made for changes of persulphate concentration (2).

The results, shown in Fig. 4, indicate that here the modulus increases more rapidly than the effective degree of cross-linking. In this respect the results for GR-S appear to differ from those obtained by Flory (6) with butyl rubber ($g = 3.3$ and 2.1), also shown in Fig. 4 together with the predictions of several elasticity theories. Of the various theories, that of Kuhn appears to be in best agreement with the experimental results for GR-S except at relatively high concentrations of cross-linkages. The hypothesis of Kuhn (23) and of

Flory (6) that other restraints in addition to chemical cross-linkages exist along the chains appears to be qualitatively correct.

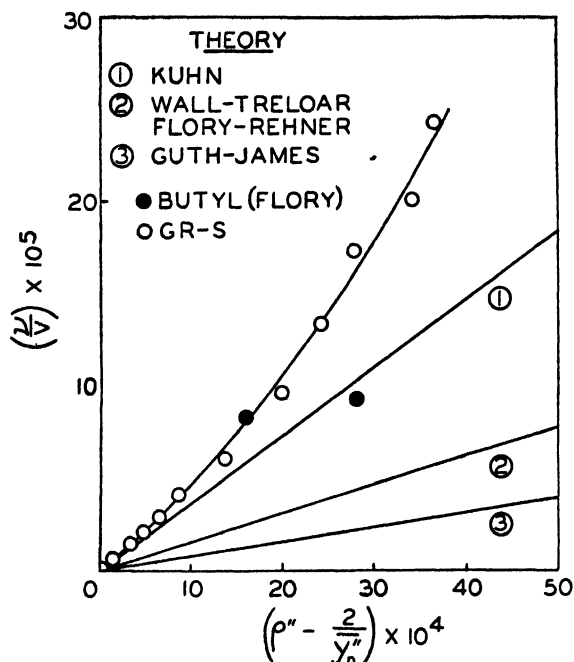


FIG. 4. Network activity vs. effective degree of cross-linking. Comparison of experimental results for GR-S and for butyl rubber (Flory) with elasticity theories.

Estimation of Primary Molecular Weight

The simple dependence of swelling volume on network structure discussed above may be exploited to *reveal* the molecular weight of the polymer from which a gel was formed. Rearranging Equation (5) gives:

$$\bar{M}_n = \frac{gd \left\{ \bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n''} \right) \right\}}{\frac{\nu}{\bar{V}}},$$

\bar{M}_n = number average primary molecular weight.

The term in parentheses in the numerator of this expression may be calculated from the solubility (1, Fig. 4) and the denominator from the swelling volume [Equation (2)]. Use of the empirical value of about 2.5 for g then permits estimation of the primary molecular weight, i.e., the molecular weight in the entire absence of cross-linkages. A few examples of the use of this novel method will be given.

(1) *Commercial GR-S*.—A GR-S latex of 70% conversion modified by commercial dodecyl mercaptan was treated with potassium persulphate (2), and the solubility and swelling of the resulting gels interpreted as in the preceding section. [The form of the primary distribution to be expected in such a polymer corresponds to about 90% modifier depletion (16)]. In

Fig. 5, $\frac{\nu}{\bar{V}}$ is plotted vs. $\bar{y}_n \left(\rho'' - \frac{2}{\bar{y}_n} \right)$. The slope of the resulting line is 4.7×10^{-5} from which \bar{M}_n , the primary molecular weight, may be estimated at about 50,000.

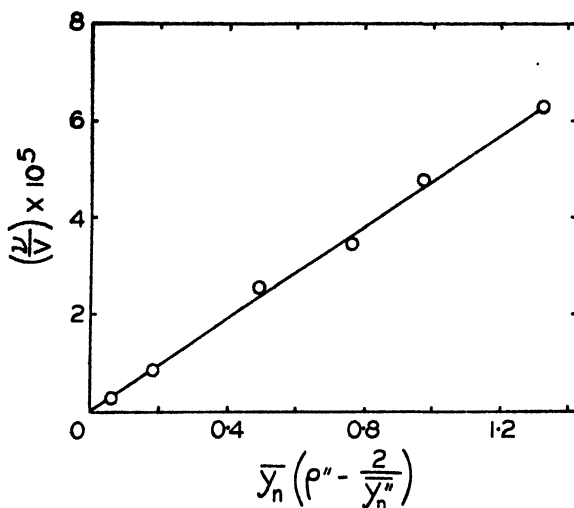


FIG. 5. Network activity vs. number of effective chains per primary molecule.

(2) *Natural Rubber*.—Since rubber in the native state generally contains a gel fraction, its primary molecular weight prior to degradation may be estimated roughly by the method under discussion. For this purpose it was assumed that the network structure of natural rubber and of GR-S are similar, i.e., a value of 2.5 was used for g . The coefficient μ_g for natural rubber in benzene was estimated at about 0.33. Measurements of the solubility and swelling of dried films of natural rubber yielded values of the order of 300,000 for the primary molecular weight.

(3) *Heat-softened GR-S*.—The gel fraction of essentially insoluble (unmodified) GR-S or Buna-S may be substantially reduced by heating in air or oxygen. An experimental study of such reactions was made in this laboratory by Dr. T. A. Eastwood (5): Oxygen at 100° C. was passed over the finely divided polymer and the changes of gel fraction and swelling index measured. (The swelling index is defined as the *weight* ratio of swollen to dried gel.) Typical results are shown in Fig. 6. It is seen that the gel fraction falls initially, but rises as the treatment is prolonged. Similar trends have been observed by Cole and Field (4).

From these results the primary chain length, \bar{y}_n and the degree of cross-linking, ρ , were calculated. In Fig. 6 the reaction is resolved into its cross-linking and scission components by plotting ρ and $\frac{1}{\bar{y}_n}$ against time of reaction. This analysis suggests that both scission and cross-linking are proceeding at comparable rates. During the initial part of the reaction, scission is slightly

avored, but is subsequently overtaken by the cross-linking process. On this basis there is no reason to believe that heat-softening proceeds through specific attack by oxygen at the chemical cross-linkages.

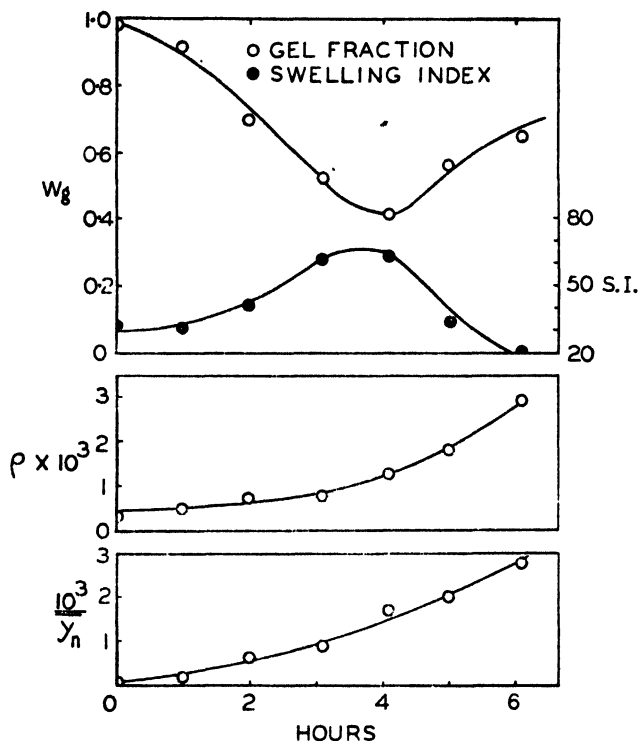


FIG. 6. Relative rates of cross-linking and scission during heat-softening.

Conclusions

In the correlation between elastic properties and network structure it is the influence of molecular weight that is of greatest practical importance. This effect stems from the fact that each end of a primary molecule results in a "flaw" which impairs the properties of the final network (8, 10). The low value of the primary molecular weight of GR-S as now produced indicates that such "flaws" may be quite prevalent in its vulcanizates.

It is to be noted that for satisfactory correlation of elastic properties with molecular weight it is the *primary* rather than the actual molecular weight that should be considered. When cross-linking reactions accompany chain growth the resulting polymer contains "clusters" of molecules which severely distort the *actual* molecular weight distribution. The weight average molecular weight is greatly affected by the presence of such clusters (9, 29). Their influence is revealed by empirical expressions for the viscosity molecular weight (16) which show that in the neighborhood of the gel point only a small fraction of the viscosity is due to the lengths of the *primary* molecules. For this reason good correlation of elastic properties with viscosity molecular weight can scarcely be expected.

The effect of *distribution* of primary molecular weight on elastic properties may be discussed in terms of the increase in number of effective chains during cure (1, Fig. 3). For a given number average primary chain length a fixed degree of cross-linking leads to a slightly greater fraction of effective chains with the more *heterogeneous* polymer. In practice however this advantage of heterogeneity may be offset to some extent by the increased difficulties of processing.

Acknowledgments

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MOLECULAR WEIGHTS FROM MICRO QUANTITIES OF MATERIALS¹

BY I. E. PUDDINGTON

Abstract

A method is proposed for the determination of the molecular weight of chemical compounds in which the unknown substance may be used successfully in quantities of 1 mgm. or less. The method depends on the accurate measurement of the difference in vapor pressure between a solution of the unknown compound and the pure solvent, and this is accomplished with a modified mercury U-tube manometer. The results presented indicate that the difference between the experimental and theoretical molecular weights is of the order of 2%. Determinations require from two to three hours and the sample may be recovered.

Introduction

The work of Frazer and others (1, 2) in the few years following 1914 showed that static measurements of the vapor pressure of pure solvents and solutions could be made with considerable precision. Their work also showed that the vapor pressure of solutions of several nonionizing chemical compounds could be predicted by Raoult's law, even at quite high solute concentrations. However, this method of approach has not become popular for the estimation of molecular weights, despite the obvious advantage that vapor pressures can be measured over a range of temperature and are not subject to superheating and undercooling effects. The possibility of this method being used where only small quantities of material are available has prompted the present investigation.

At low molecular concentrations Raoult's law may be written in the form

$$m = w \cdot \frac{M}{W} \cdot \frac{P}{P - P_0},$$

where m and w are the molecular weight and mass of solute present, M and W are the molecular weight and mass of the solvent used, while P and P_0 are the vapor pressures of the solvent and solution measured at the same temperature. In the determination of molecular weights P and $P - P_0$ are the quantities observed. P is normally large enough to be measured directly with an ordinary mercury manometer, but since $P - P_0$ is the difference between two relatively large quantities, it is preferable to measure this difference by a sensitive differential method rather than attempt to measure P and P_0 .

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absolutely to the required degree of precision. The pressure differential, $P - P_0$, can be increased by working at elevated temperatures or by using solvents with high vapor pressures. These restrictions frequently lead to other difficulties, however, and the work reported here has been done a few degrees below room temperature, using solvents with relatively low vapor pressures.

Experimental

The apparatus, which is similar to one used in previous investigations, where its operation was described (4, 5) is shown in Fig. 1. Linear displacement of a mercury thread in the uniform capillary *A* indicates pressure changes at the

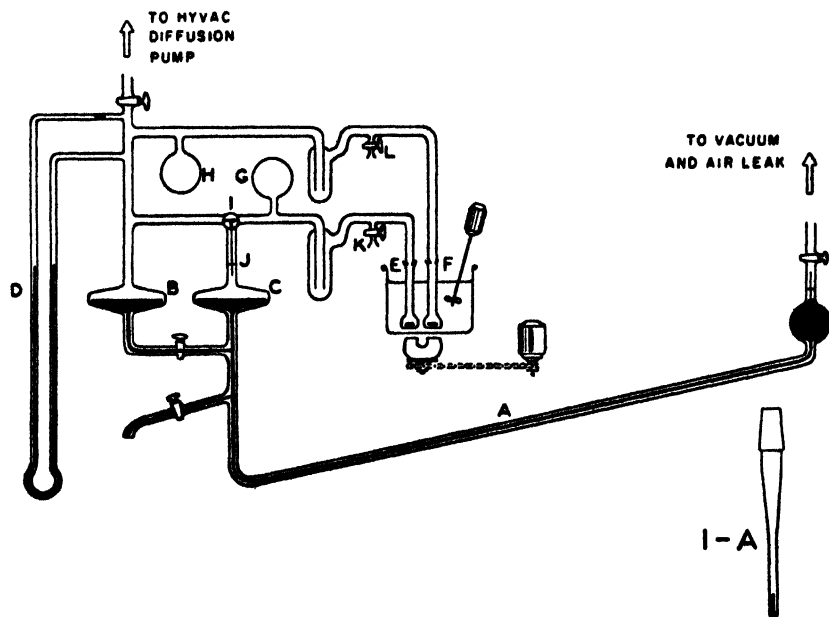


FIG. 1. *Apparatus.*

enlargements in the U-tube mercury manometer, *B* and *C*, with a magnification of 1650. Since the mean value of a group of readings on *A* can be reproduced to within ± 1 mm., values of actual vapor pressure differences between solvent and solution which are impressed at *B* and *C* should be good to about 0.001 mm. The vapor pressure of the pure solvent is recorded on the manometer *D*. Solution and solvent are contained in the sample holders *E* and *F*, which are partially immersed in a thermostat.

In the initial work on the problem, solutions were made up gravimetrically and about 0.5 cc. of solvent and solution placed in their respective sample holders. Both samples were then freed from air by vacuum distilling the solvent to the traps and back to the sample holders several times, using a suitable refrigerant to prevent loss of solvent. The pressure in the system was reduced to about 10^{-5} mm. between each distillation. Both solvent and solution were stirred by placing small, glass enclosed, alnico magnets in the

sample holders and rotating a large horseshoe magnet slowly under the thermostat, as indicated in Fig. 1. Gradually decreasing values of the measured vapor pressure differences with successive readings, which were noted in early runs, were eventually traced to small amounts of permanent gases that were not removed by the vacuum distillations and came out of solution slowly, during a determination. This difficulty was overcome by adding 100 cc. of dead space to each side of the manometer at *G* and *H*, thus diluting the permanent gases to insignificant pressures. Corrections for the increased concentration of the solution, due to the volume of vapor, then became necessary. When the solvents used were water, ethyl alcohol, and acetone, a stopcock grease composed of 25% of lithium stearate dispersed in an oil with a viscosity of 3500 S.U.S. at 100° F. (3), was quite satisfactory. If, however, hydrocarbon solvents are required it would be necessary to use a glycerine-silica lubricant (6) or to substitute mercury cutoffs for the stopcocks.

For ordinary work, precise thermostatic control is not required. It is only necessary that the solution and solvent be kept at the same temperature; its absolute value is not important. The drift in the temperature of a liter beaker filled with water at about 2° C. below room temperature was found to be only a few tenths of a degree per hour, and this type of water bath was used to obtain most of the data reported in Table I. If a thermostat is used, the manometer *D* may be dispensed with, and the literature values for the vapor pressure of the pure solvent used.

Equilibrium is reached quickly, and measurements of the vapor pressure lowering may be taken at 15 to 20 min. intervals. Since the zero point of the manometer is a function of the room temperature, it is advisable to check it after each reading by turning the three way stopcock *I* to connect *B* and *C*. If this is done after the mercury has been adjusted to the etch at *J* no dilution of the sample takes place.

The preliminary results, which are presented in Table I, were sufficiently encouraging to warrant extending the work to smaller samples, and the apparatus was modified accordingly. The ballast bulbs *H* and *G* were sealed off to reduce the volume, and sample holders of the form shown in large scale in Fig. 1-A were prepared. These were made by sealing about 5 cm. of 2 mm. I.D. tubing to $\frac{12}{30}$ S.T. ground glass joints. Stirring of solvent and solution was accomplished by placing a piece of a glass enclosed iron nail, about 1 cm. long and 0.8 mm. diameter, in the tubes and passing a small magnet vertically past the sample holders about 200 times per minute. This caused the stirrers to execute a "hula dance", which produced good agitation.

The samples of solute were weighed directly into the sample holders on a microbalance and after these were placed in position, the whole apparatus was evacuated to a pressure of 10^{-5} mm. Weighed samples of solvent (about 20 to 40 mgm.) were then attached at the ground glass joints *L* and *K* and distilled into the system through the stopcocks. Dissolved permanent gases were removed by reducing the pressure while the solvent was held in the traps

absolutely to the required degree of precision. The pressure differential, $P - P_0$, can be increased by working at elevated temperatures or by using solvents with high vapor pressures. These restrictions frequently lead to other difficulties, however, and the work reported here has been done a few degrees below room temperature, using solvents with relatively low vapor pressures.

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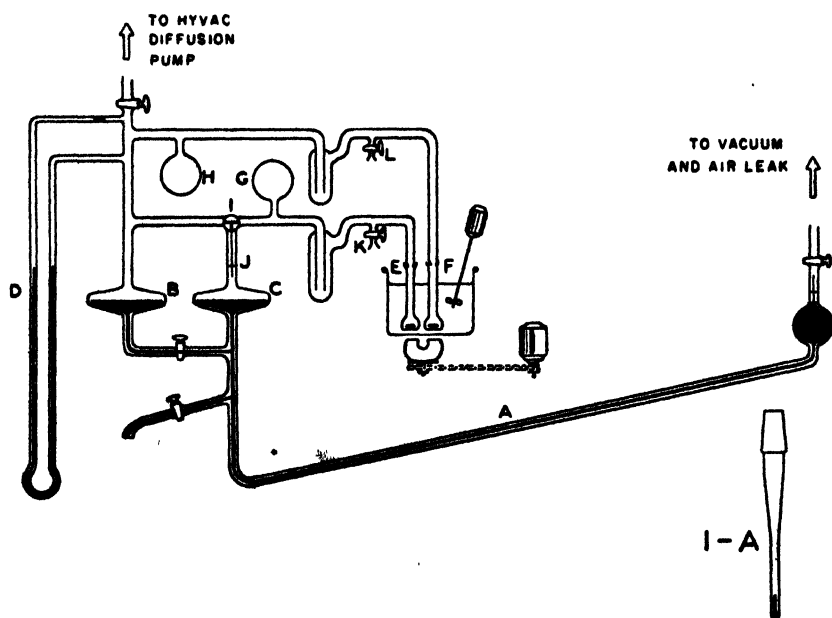


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In the initial work on the problem, solutions were made up gravimetrically and about 0.5 cc. of solvent and solution placed in their respective sample holders. Both samples were then freed from air by vacuum distilling the solvent to the traps and back to the sample holders several times, using a suitable refrigerant to prevent loss of solvent. The pressure in the system was reduced to about 10^{-5} mm. between each distillation. Both solvent and solution were stirred by placing small, glass enclosed, alnico magnets in the

sample holders and rotating a large horseshoe magnet slowly under the thermostat, as indicated in Fig. 1. Gradually decreasing values of the measured vapor pressure differences with successive readings, which were noted in early runs, were eventually traced to small amounts of permanent gases that were not removed by the vacuum distillations and came out of solution slowly, during a determination. This difficulty was overcome by adding 100 cc. of dead space to each side of the manometer at *G* and *H*, thus diluting the permanent gases to insignificant pressures. Corrections for the increased concentration of the solution, due to the volume of vapor, then became necessary. When the solvents used were water, ethyl alcohol, and acetone, a stopcock grease composed of 25% of lithium stearate dispersed in an oil with a viscosity of 3500 S.U.S. at 100° F. (3), was quite satisfactory. If, however, hydrocarbon solvents are required it would be necessary to use a glycerine-silica lubricant (6) or to substitute mercury cutoffs for the stopcocks.

For ordinary work, precise thermostatic control is not required. It is only necessary that the solution and solvent be kept at the same temperature; its absolute value is not important. The drift in the temperature of a liter beaker filled with water at about 2° C. below room temperature was found to be only a few tenths of a degree per hour, and this type of water bath was used to obtain most of the data reported in Table I. If a thermostat is used, the manometer *D* may be dispensed with, and the literature values for the vapor pressure of the pure solvent used.

Equilibrium is reached quickly, and measurements of the vapor pressure lowering may be taken at 15 to 20 min. intervals. Since the zero point of the manometer is a function of the room temperature, it is advisable to check it after each reading by turning the three way stopcock *I* to connect *B* and *C*. If this is done after the mercury has been adjusted to the etch at *J* no dilution of the sample takes place.

The preliminary results, which are presented in Table I, were sufficiently encouraging to warrant extending the work to smaller samples, and the apparatus was modified accordingly. The ballast bulbs *H* and *G* were sealed off to reduce the volume, and sample holders of the form shown in large scale in Fig. 1-A were prepared. These were made by sealing about 5 cm. of 2 mm. I.D. tubing to $\frac{12}{30}$ S.T. ground glass joints. Stirring of solvent and solution was accomplished by placing a piece of a glass enclosed iron nail, about 1 cm. long and 0.8 mm. diameter, in the tubes and passing a small magnet vertically past the sample holders about 200 times per minute. This caused the stirrers to execute a "hula dance", which produced good agitation.

The samples of solute were weighed directly into the sample holders on a microbalance and after these were placed in position, the whole apparatus was evacuated to a pressure of 10^{-5} mm. Weighed samples of solvent (about 20 to 40 mgm.) were then attached at the ground glass joints *L* and *K* and distilled into the system through the stopcocks. Dissolved permanent gases were removed by reducing the pressure while the solvent was held in the traps

with a refrigerant. It was relatively easy to remove the gases from the small quantities of solvent used, and two cycles of evaporating and condensing were usually enough. The solution was finally prepared by condensing the solvent into the sample holder and stirring. For this work the temperature of the thermostat was held close to 20° C. and was sufficiently constant that no variation could be observed on a Beckmann thermometer over periods of several hours. The volume of the dead space on the solution side of the manometer was determined by expanding a known volume of air at a predetermined pressure into it and noting the resulting pressure. This made it possible to correct the solution concentration for the solvent in the vapor phase.

An alternative method of introducing the solvent, which produced good results, is as follows. The solvent is boiled in a flask fitted with a stopcock and ground glass joint until dissolved gases are removed. The stopcock is then closed and the flask attached to the apparatus, leaving the solvent stored, air-free, in the liquid state. Known amounts may be admitted to the evacuated system through *K* and *L*, by measuring the pressure of the solvent while it is in the vapor phase, in a calibrated volume. This scheme requires some additional apparatus that is not indicated in Fig. 1.

The vapor pressure differences between solvents and solutions were measured in the usual way with the differential manometer, and the molecular weights of the solutes calculated from Raoult's law.

Results and Discussion

The experimental results are presented in Tables I and II. Individual values of consecutive measurements are given to indicate the spread obtained in the data.

Apparently the micromethod is capable of as high a degree of precision as can be obtained when larger quantities are used. This is not too surprising since the chief source of error lies in the failure to remove the last traces of dissolved gases in the solvent, and it is easier to remove these from 30 than from 500 mgm. Also, drafts in the room can also cause brief pressure changes in the ballast bulbs required for the larger samples and lead to errors that do not occur with the micro samples.

With the last three examples cited in Table II the solvent was measured and introduced in the vapor state. When such small samples as this are used, some added precautions are necessary. In addition to reducing the pressure within the apparatus to a "click" vacuum on a McLeod gauge prior to introducing the solvent, it is desirable to expose the inside of the apparatus and the solute sample to the solvent vapor at a pressure somewhat less than the vapor pressure of the solvent, followed by reducing the pressure to a "click" vacuum once again before the solution is prepared. This treatment removes adsorbed air and water vapor, which would give trouble in the subsequent determination. Another precaution that was found necessary when absolute alcohol was used as a solvent arose from the fact that the alcohol was only about 99% C_2H_5OH .

TABLE I
MOLECULAR WEIGHT DETERMINATIONS

Solute	Amount used, mgm.	Solvent	Thermostat	Molecular weight	
				Theoretical	Experimental
Mannitol	14	Water	Uncontrolled	182	181 181 184 189 Av. 184
Triphenyl phosphate	9	Absolute alcohol	Uncontrolled	333	328 326 330 Av. 328
Stearic acid	8	Absolute alcohol	Uncontrolled	284	285 291 292 Av. 289
Triphenyl phosphate	3	Acetone	Automatic	333	328 321 340 350 Av. 335
Stearic acid	2	Acetone	Automatic	284	280 291 296 296 Av. 291

To reduce the slight fractionation that occurred on the solvent side of the manometer, where the dead space was larger, to insignificant proportions, it was necessary to use at least as much solvent as the solution contained.

In the last example in Table II the value of $P - P_0$ was less than 0.02 mm. and the total spread of all four readings was only 0.0011 mm. This indicates the precision that can be obtained with the manometer.

From the formula given, relating the molecular weight to vapor pressure lowering, it is obvious that for a given weight concentration of solute $P - P_0$ will be proportional to the product of P and M . Thus if it were possible to use both water and ethyl ether as solvents for a determination at 20° C., only about 0.01 of the weight concentration used with the water would be required for the ether solution to give the same $P - P_0$. This point is illustrated in Table I, where decreasing quantities of solute are used in passing from the solvents with low to those of higher vapor pressures. However, since other sources of error such as the increased effect of fluctuations in room temperature

TABLE II

MOLECULAR WEIGHTS FROM MICROSAMPLES

Solute	Amount used, mgm.	Solvent	Molecular weight	
			Theoretical	Experimental
Mannitol	1.207	Water	182	182 181 181 183
				Av. 182
Palmitic acid	0.882	Absolute alcohol	256	254 261 258
				Av. 258
Triphenyl phosphate	0.818	Absolute alcohol	333	350 347 338
				Av. 345
Triphenyl phosphate	0.218	Absolute alcohol	333	324 320 326
				Av. 324
Yohimbine	0.137	Absolute alcohol	354	410 350 365 357 357
				Av. 368
Yohimbine	0.095	Absolute alcohol	354	355 344 367 355
				Av. 355

and higher temperature coefficients of vapor pressure become more important as the vapor pressure increases, it is probably preferable to keep the molecular concentration of solute about the same for the two solvents and use a less sensitive manometer than has been used here.

Another important consideration is the chemical stability of the solvent. Water and alcohol are very good in this respect but acetone must be used with care. Reasonably good results may be obtained with it, as Table I shows, if the vapor pressures are measured as soon as possible after the solutions are made up, but very real changes in vapor pressure appear to take place if the acetone solutions are allowed to stand. This is probably due to photochemical reactions and the effect may be exaggerated with the dilute solutions and highly sensitive differential pressure measurements used here.

The method as described should be of considerable use especially where the amount of material available is limited. While setting up the apparatus initially may be somewhat complicated, once built, the assembly is permanent, and a determination may be made in two to three hours. The samples are, of course, completely recoverable.

Work is now in progress to extend the molecular weight range to include polymers.

Acknowledgment

The many helpful discussions that were held with Dr. L. Marion during the progress of this work, and the technical assistance of Mr. J. F. Eagen, who made the micro weighings referred to in the text, are gratefully acknowledged.

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SOME ANOMALOUS REACTIONS OF PHENYLMAGNESIUM CHLORIDE¹

BY RICHARD H. F. MANSKE AND ARCHIE E. LEDINGHAM

Abstract

When phenylmagnesium chloride is prepared from magnesium in chlorobenzene without the aid of another solvent, there is formed not only the expected diphenyl in addition to the phenylmagnesium chloride but also tractable amounts of xenyl- and terphenyl-magnesium chlorides. The presence of these substances for the formation of which a mechanism is not suggested was proved by the isolation of *p*-xenylethyl alcohol, *p*-terphenylethyl alcohol, and *p*-phenylbenzoic acid when the Grignard compounds were treated with appropriate reagents.

In the course of a study of the preparation of phenylmagnesium chloride in chlorobenzene without the aid of another solvent it was observed that products other than diphenyl and the desired Grignard compound were obtained. When the mixture was treated with ethylene oxide there was obtained a fair yield of phenylethyl alcohol and a higher boiling fraction from which it was possible to isolate terphenyl and *p*-xenylethyl alcohol. Kharasch and Fields (2) have drawn attention to a free radical mechanism which accounts for the formation of the higher condensed hydrocarbons such as terphenyl, quadriphenyl, etc. These authors however do not mention the formation of *p*-xenylmagnesium halides and their homologues. That such occur under the present experimental conditions was proved by the isolation not only of *p*-xenylethyl alcohol but also of *p*-terphenylethyl alcohol. Furthermore, when the Grignard mixture was carbonated the resulting acids consisted of a mixture of benzoic acid and *p*-phenylbenzoic acid.

Owing to the pressure of other work the present results are submitted without attempts to propose a mechanism. For the greater part, the magnesium used in these experiments was a sample of the distilled metal which was kindly placed at our disposal by Dr. L. M. Pidgeon, The University, Toronto, Ont. Experiments in which the magnesium had been alloyed with cobalt or with copper to increase its activity did not materially affect the results.

Experimental

Phenylmagnesium Chloride

Fresh magnesium borings (72 gm.) and monochlorobenzene (1000 gm.) were heated to boiling in a three liter flask fitted with a mercury seal stirrer and a reflux condenser fitted with a drying tube. Dissolution of the magnesium usually began after about 10 min. of boiling. In some experiments it was necessary to start the reaction by the addition of a crystal of iodine. With fine borings obtained by the use of a sharp drill, the magnesium had dissolved virtually completely in 10 hr.

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

Phenylethyl Alcohol

A solution of ethylene oxide (99 gm.) dissolved in chlorobenzene (400 gm.) was added to the Grignard reagent prepared as above at such a rate that the temperature did not exceed 35° C. A cooling bath of iced water was sufficient to maintain this temperature if the addition time was of the order of one hour. If the cooling is not maintained, a second more pronounced exothermal reaction takes place and the mixture sets to a firm gel which cannot be stirred. When all the ethylene oxide had been added the cooling bath was removed. A spontaneous reaction then ensued during which the temperature rose to 80° C. To complete the rearrangement the flask was immersed in a boiling water bath for one hour. After cooling to room temperature the resultant firm gel was decomposed with dilute sulphuric acid and the mixture filtered to facilitate subsequent separation of the liquid layers. The chlorobenzene solution was washed with water, the solvent removed under reduced pressure, and the residue fractionated *in vacuo*. The main fraction distilled at 100° to 120° C. (12 mm.) and consisted chiefly of phenylethyl alcohol, contaminated with some diphenyl with which it forms a constant boiling mixture. The yield was 185 gm.

Xenylethyl Alcohol and Terphenyl

The residue from the phenylethyl alcohol was subjected to further fractionation *in vacuo* and the fraction boiling at 160° to 180° C. (2 mm.) fractionally crystallized from benzene-hexane. From 50 gm. of such a fraction a small amount of a sparingly soluble material separated which when recrystallized several times, melted sharply at 213° C.* Terphenyl is stated to melt at 209° C. uncorrected (1) and the analytical figures indicate that the compound was terphenyl. Calc. for $C_{18}H_{14}$: C, 93.91; H, 6.09%. Found: C, 93.97; H, 6.22%.

The mother liquors from the terphenyl on concentrating and chilling, and repeated recrystallization from benzene-hexane, yielded some *p*-xenylethyl alcohol melting sharply at 94° C. (4). Calc. for $C_{14}H_{14}O$: C, 84.85; H, 7.07%. Found: C, 84.60, 84.61; H, 6.73, 6.87%.

When the *p*-xenylethyl alcohol was treated under anhydrous conditions with phenylisocyanate it yielded the corresponding *urethane* which when recrystallized from benzene-hexane consisted of colorless needles melting at 103° C. Calc. for $C_{21}H_{18}O_2N$: N, 4.43%. Found: N, 4.34%.

Terphenylethyl Alcohol

A higher boiling fraction (180° to 220° C. (2 mm.)) from the phenylethyl alcohol preparation solidified partly on standing. When the separated solid was recrystallized several times from benzene it was obtained in colorless plates melting at 224° to 225° C. That it is *p*-terphenylethyl alcohol is confirmed

* All melting points are corrected.

by its analysis, although there was insufficient for the preparation of a derivative. Calc. for $C_{20}H_{18}O$: C, 87.59; H, 6.57%. Found: C, 87.27, 87.39; H, 6.22, 6.35%.

Benzoic Acid and Phenyl Homologues

The Grignard reagent as prepared above was diluted with sufficient dry ether to render the mixture mobile enough to pour on to an excess of solid carbon dioxide. When the excess carbon dioxide had evaporated, the mixture was acidified with dilute hydrochloric acid and filtered. The washed organic layer was then extracted with aqueous sodium carbonate and the acids regenerated from the aqueous extract.

The product thus obtained consisted substantially of benzoic acid but there was present a small portion only very sparingly soluble even in boiling water. This portion was collected from several runs and esterified with methanol and sulphuric acid, and the ester fractionated *in vacuo*. The low boiling fraction (70° to 100° C. (2 mm.)) consisted largely of methyl benzoate.

A second fraction collected at 150° to 170° C. (2 mm.) solidified for the greater part and when recrystallized from methanol consisted of large colorless plates melting at 117° C. (3). This is methyl *p*-phenylbenzoate. The recrystallized acid obtained by hydrolysis of the ester melted at 227° C. (3).

From a higher boiling fraction (170° to 240° C. (2 mm.)) a small amount of a compound melting at 225° to 226° C. was obtained. It consisted of pale greenish yellow fluorescent plates when recrystallized from methanol-benzene. It may consist substantially of a methyl terphenyl carboxylate. Calc. for $C_{20}H_{16}O_2$: C, 83.33; H, 5.55. Found: C, 82.08, 82.44; H, 5.76, 5.90%.

Diphenyl and Terphenyl

The alkali insoluble portion from the preparation of the benzoic acid was distilled *in vacuo* and the fraction boiling at 100° to 120° C. (5 mm.) after being recrystallized from methanol melted at 69° C. either alone or in admixture with diphenyl.

A second fraction collected at 160° to 220° C. (5 mm.) when recrystallized from benzene-hexane melted at 213° C. either alone or in admixture with a specimen of terphenyl obtained as above.

A third fraction which sublimed at 200° to 220° C. (1 mm.) when recrystallized from benzene was obtained in colorless plates melting at 300° to 305° C. The amount was insufficient for analysis but it probably consisted substantially of quaterphenyl for which Ullmann and Myer (5) give a melting point of 317° C.

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THE SYNTHESIS OF SOME ISOQUINOLINES¹

BY RICHARD H. F. MANSKE AND MARSHALL KULKA

Abstract

A number of new isoquinolines substituted in the benzene nucleus have been prepared. The substituents include hydrazino-, chloro-, nitro-, and some combinations of these.

In connection with another problem a number of hydrazinoisoquinolines were required. Two of the necessary aminoisoquinolines (5- and 7-) are already known and served as the basis for orienting a number of new compounds.

Attempts to ring close the Schiff base (I) with sulphuric acid of several concentrations at temperatures below 100° C. led to regeneration of *m*-chlorobenzaldehyde, and fluosulphonic acid caused polymer formation. However, a mixture of sulphuric acid and phosphorus pentoxide at 160° C. (6) yielded a mixture of 5- (II) and 7-chloroisoquinoline (III), the components of which could be separated by crystallization of the bases from hexane or of the perchlorates from dilute perchloric acid. The orientation of the chloro-compounds was established by comparison with the 5- and 7-chloroisoquinolines obtained via the Sandmeyer reaction from the 5- (1, 4, 5, 6) and 7-aminoisoquinolines (5), respectively.

Nitration of the 5- and 7-chloroisoquinolines yielded 5-chloro-8-nitro- (V) and 7-chloro-8-nitroisoquinolines (VI) respectively, which, when heated with ethanolic ammonia at 150° C. gave rise to the known corresponding 5-amino-8-nitro- (VIII) (3) and 7-amino-8-nitroisoquinolines (IX). An attempt to convert the latter (IX) into 8-nitroisoquinoline by treating the diazonium salt with hypophosphorous acid yielded only 8-chloroisoquinoline (X) (3). The labilization of a nitro-group by a diazonium group, to the extent that the former is replaced by chlorine in the presence of hydrochloric acid, is not new (3). When the diazonium salt of IX was treated with stannous chloride in hydrochloric acid it yielded 7-hydrazino-8-chloroisoquinoline (XI).

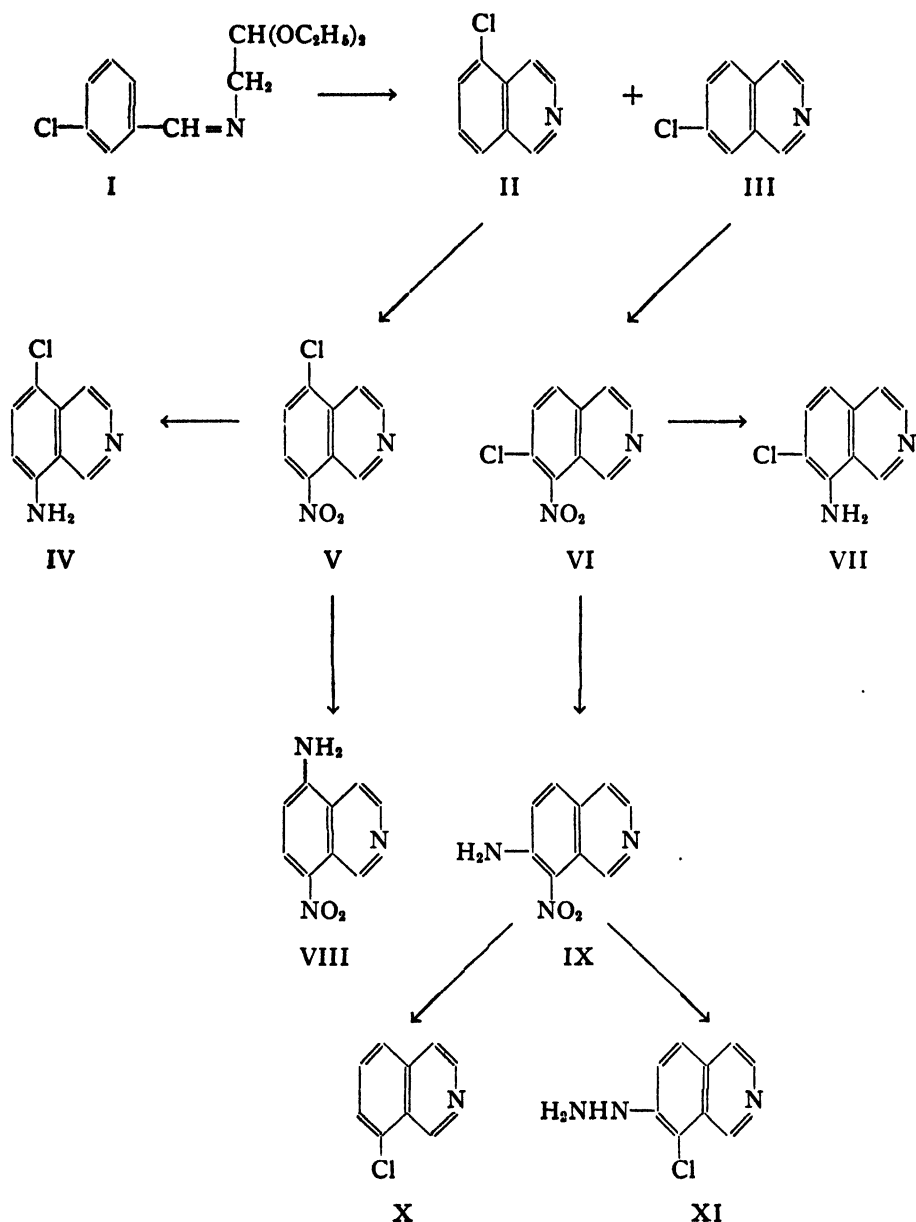
Direct chlorination of 7-acetylaminoisoquinoline gave erratic results and only in one experiment was it possible to isolate a homogeneous substance which upon deacetylation and elimination of the amino-group yielded 8-chloroisoquinoline. That the chlorine entered the 8-position is further confirmed by the observation that the hydrazinoisoquinoline prepared from it was identical with XI obtained as above. Nitration of 7-acetylaminoisoquinoline yielded only tarry products.

An attempt to prepare 7-amino-8-chloroisoquinoline from 7-hydroxy-8-chloroisoquinoline by the Bucherer reaction yielded chiefly 7-aminoisoquino-

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

line, the halogen having been eliminated. The necessary hydroxy-chloro compound was prepared by ring closure of the Schiff base from 2-chloro-3-hydroxybenzaldehyde and aminoacetal.



Experimental

7-Aminoisoquinoline

This was prepared from 7-hydroxyisoquinoline according to the method of Robinson (5). In the preparation of 7-hydroxyisoquinoline (7) better yields were obtained when the Schiff base of *m*-hydroxybenzaldehyde and aminoacetal was purified before cyclization. Acetylation with acetic anhydride in

acetic acid yielded 7-acetylaminoisoquinoline; m.p. 147° to 148° C.,* from benzene. Calc. for $C_{11}H_{10}N_2O$: C, 70.98; H, 5.38; N, 15.06%. Found: C, 70.72, 70.92; H, 5.44, 5.42; N, 14.64%.

The hydrate melts at 103° to 104° C.

5- and 7-Hydrazinoisoquinoline

A solution of 5-aminoisoquinoline (4) (14.4 gm.) in concentrated hydrochloric acid (50 cc.) and water (75 cc.) was diazotized with a solution of sodium nitrite (6.9 gm.) in water (50 cc.), the temperature being kept below 0° C. The diazonium salt solution was then added to a cold solution of stannous chloride dihydrate (50 gm.) in concentrated hydrochloric acid (75 cc.) with stirring over a period of about 15 min. the temperature being maintained at 10° C. by cooling. Then the reaction mixture was allowed to stand for two hours, the yellow precipitate filtered, and the filtrate concentrated to ca. 50 cc. under reduced pressure, and cooled. The yellow precipitate was again filtered. The combined precipitates were dissolved in 500 cc. of hot water and the solution saturated with hydrogen sulphide. The tin sulphide was filtered off, washed with water, the combined filtrate and washings concentrated to ca. 100 cc. under reduced pressure, and the concentrate basified with ammonium hydroxide. The precipitated 5-hydrazinoisoquinoline was filtered, washed, and crystallized from ethanol; white needles, m.p. 165° to 167° C.; yield, 8.1 gm. or 51%. Calc. for $C_9H_9N_3$: C, 67.92; H, 5.65; N, 26.40%. Found: C, 67.67, 67.87; H, 5.59, 5.77; N, 26.01, 25.96%.

7-Hydrazinoisoquinoline was prepared similarly from 7-aminoisoquinoline; orange prisms from benzene, m.p. 158° to 160° C.; yield, 50%. Calc. for $C_9H_9N_3$: C, 67.92; H, 5.66; N, 26.40%. Found: C, 67.90, 67.86; H, 5.87, 6.06; N, 25.80, 25.81%.

5- (II) and 7-Chloroisoquinolines (III)

(a) From the Aminoisoquinolines

A solution of 5-aminoisoquinoline (4.8 gm.) in concentrated hydrochloric acid (10 cc.) and water (25 cc.) was diazotized with a solution of sodium nitrite (2.3 gm.) in water (15 cc.) at 0° C. This was then added to a solution of cuprous chloride (4.0 gm.) in concentrated hydrochloric acid (40 cc.) previously warmed to ca. 75° C. The resulting solution was allowed to stand at room temperature overnight and then basified with sodium hydroxide and steam distilled. The solid material was separated from the steam distillate and dried; yield, 3.3 gm. or 60%; crystallized from petroleum ether (b.p. 30° to 50° C.), white needles, m.p. 73° to 74° C. Calc. for C_9H_8NCl : C, 66.05; H, 3.67; N, 8.56%. Found: C, 66.31, 66.38; H, 3.72, 3.83; N, 8.56; 8.16%.

7-Chloroisoquinoline (III) was prepared similarly; m.p. 44° to 45° C., from petroleum ether; literature (5), 45° C. Perchlorate, white needlelike crystals

* All melting points are corrected.

from methanol – ethyl acetate; m.p. 163° to 164° C. Calc. for $C_9H_7NCl_2O_4$: C, 40.95; H, 2.65%. Found: C, 41.02, 41.20; H, 3.09, 3.15%.

(b) *From m-Chlorobenzaldehyde*

A solution of *m*-chlorobenzaldehyde (2) (25 gm.) and aminoacetal (25 gm.) was heated on the steam bath for one-half hour and then distilled. The Schiff base was an almost colorless liquid distilling at 170° C. (11 mm.); yield, 42 gm. or 86%. Calc. for $C_{13}H_{18}NO_2Cl$: C, 61.04; H, 7.05%. Found: C, 60.87, 60.92; H, 7.16, 7.01%.

The Schiff base (50 gm.) was added over a period of 15 min. to stirred concentrated sulphuric acid (250 cc.), the temperature being kept at 5° C. by cooling. The resulting solution was then added, over a period of five minutes, to a stirred mixture of concentrated sulphuric acid (25 cc.) and phosphorus pentoxide (75 gm.) heated at 150° to 160° C. The dark solution was heated for 25 min. longer, cooled, diluted with water, and steam distilled in order to remove *m*-chlorobenzaldehyde (3.5 gm.), a product of hydrolysis. The acid solution was basified with sodium hydroxide and steam distilled, yielding an oily mixture of the chloroisoquinolines (8.0 gm. or 25%) which solidified on cooling. Crystallization from petroleum ether (b.p. 30° to 50° C.) yielded 4.2 gm. of 5-chloroisoquinoline; m.p. 72° to 73° C. The filtrate was taken to dryness, the residue dissolved in 15 cc. of warm 30% perchloric acid, and the solution cooled, yielding 1.2 gm. of the needlelike crystals of the perchlorate of 7-chloroisoquinoline, m.p. 162° to 163° C. The perchloric acid filtrate was basified, the precipitated oil extracted with ether, the ether removed and the residue subjected to further alternate crystallizations from petroleum ether and 30% perchloric acid. In this way there was obtained 5.3 gm. of 5-chloroisoquinoline and 1.6 gm. of the 7-chloroisoquinoline perchlorate.

In a smaller scale run (5 gm. of the Schiff base) the yield of the mixed chloroisoquinolines was 38% and the two components were present in about equal quantities.

5- (V) and 7-Chloro-8-nitroisoquinolines (VI)

To a solution of 5-chloroisoquinoline (16.5 gm.) in concentrated sulphuric acid (120 cc.) was added with stirring a solution of potassium nitrate (12 gm.) in concentrated sulphuric acid (100 cc.) over a period of about five minutes. The temperature was maintained at 20° to 25° C. After allowing the reaction mixture to stand at room temperature for one hour, it was poured on ice and basified with ammonium hydroxide. The yellow precipitate was filtered, washed with water, air-dried, and crystallized from methanol or benzene; light-yellow needles, m.p. 134° to 135° C.; yield, 17.8 gm. or 87%. Calc. for $C_9H_6N_2O_2Cl$: C, 51.78; H, 2.40; N, 13.43%. Found: C, 51.97, 52.01; H, 2.63, 2.76; N, 13.74, 13.75%.

7-Chloroisoquinoline was nitrated in a similar manner, giving an 85% yield of 7-chloro-8-nitroisoquinoline (VI); light-yellow needles from methanol, m.p. 146° to 147° C. Calc. for $C_9H_6N_2O_2Cl$: C, 51.78; H, 2.40; N, 13.43%. Found: C, 52.07, 52.10; H, 2.55, 2.63; N, 13.23, 13.12%.

5- (VIII) and 7-Amino-8-nitroisoquinolines (IX)

A solution of 5-chloro-8-nitroisoquinoline (V) (0.5 gm.) in absolute ethanol (75 cc.) containing ammonia (10 gm.) was heated at 150° C. in a 500 cc. hydrogenation bomb for 18 hr. The reaction mixture was taken to dryness and the residue crystallized from ethanol; orange needles, m.p. 265° to 268° C. (with decomposition). This was acetylated, yielding 5-acetylamino-8-nitroisoquinoline; m.p. 225° to 227° C.; literature, 228° C. (3).

7-Chloro-8-nitroisoquinoline (VI) was aminated similarly, yielding 7-amino-8-nitroisoquinoline (IX) (65%); orange needles, m.p. 246° to 247° C. from ethanol. Calc. for $C_9H_7N_3O_2$: C, 57.14; H, 3.70; N, 22.1%. Found: C, 56.80, 57.02; H, 3.76, 3.93; N, 22.96, 22.66%.

5- (IV) and 7-Chloro-8-aminoisoquinoline (VII)

A solution of 5-chloro-8-nitroisoquinoline (V) (17.8 gm.) in concentrated hydrochloric acid (100 cc.) was added to a cold solution of stannous chloride dihydrate (50 gm.) in concentrated hydrochloric acid (100 cc.). The reaction mixture was heated on the steam bath for one hour and then evaporated to dryness under reduced pressure. The residue was dissolved in hot water (1500 cc.) and the solution saturated with hydrogen sulphide. The tin sulphides were filtered and washed well with hot water in order to remove the sparingly soluble dihydrochloride. The combined filtrate and washings were basified with sodium hydroxide, the white voluminous precipitate, filtered and crystallized from benzene or ethyl acetate; white woolly needles, m.p. 204° to 205° C.; yield, 11.5 gm. or 75%. Calc. for $C_9H_7N_2Cl$: C, 60.50; H, 3.92; N, 15.70%. Found: C, 60.43, 60.32; H, 4.29, 4.22; N, 15.61%.

7-Chloro-8-aminoisoquinoline (VII) was prepared similarly from 7-chloro-8-nitroisoquinoline; almost white needles, from benzene, m.p. 171° to 172° C.; yield, 55%. Calc. for $C_9H_7N_2Cl$: C, 60.50; H, 3.92; N, 15.70%. Found: C, 60.56, 60.38; H, 4.28, 3.95; N, 15.73%.

Deamination of 7-Amino-8-nitroisoquinoline

To a solution of 7-amino-8-nitroisoquinoline (0.12 gm.) in concentrated hydrochloric acid (10 cc.) was added solid sodium nitrite (0.05 gm.) and the reaction mixture stirred at 0° C. for two hours. To this was added 30% hypophosphorous acid (2 cc.) and the solution allowed to stand at 0° C. for one hour and then at room temperature for 15 hr. The yellow solution was diluted with water, basified with sodium hydroxide, and steam distilled. The oily material in the steam distillate solidified on cooling; yield, 0.05 gm.; m.p. 54° to 55° C., mixed m.p. with an authentic sample of 8-chloroisoquinoline (3), no depression.

7-Hydrazino-8-chloroisoquinoline (XI)

7-Amino-8-nitroisoquinoline (IX) (1.1 gm.) was diazotized with solid sodium nitrite (0.38 gm.) as above and to this solution was added stannous chloride dihydrate (6.0 gm.) in concentrated hydrochloric acid (20 cc.) cooled

to 0° C. The dark solution was allowed to stand at 8° C. overnight and then taken to dryness under reduced pressure. The residue was dissolved in hot water (100 cc.) and the solution saturated with hydrogen sulphide. The tin sulphides were filtered off and the filtrate basified with sodium hydroxide. The precipitated hydrazine was filtered and crystallized from benzene; golden-yellow needles, m.p. 176° to 178° C. (with decomposition); yield, 0.62 gm. or 56%. Calc. for $C_9H_8N_3Cl$: C, 55.81; H, 4.13; N, 21.70%. Found: C, 56.02, 56.02; H, 4.25, 4.11; N, 22.11%.

8-Hydrazino-5-chloroisoquinoline

This was prepared from 8-amino-5-chloroisoquinoline (IV) using the same method as that used for 7-hydrazino-8-chloroisoquinoline above; light-yellow needles, from benzene, m.p. 192° to 193° C. (with decomposition); yield, 80%. Calc. for $C_9H_8N_3Cl$: C, 55.81; H, 4.13; N, 21.70%. Found: C, 55.86, 55.57; H, 4.36, 4.58; N, 21.66%.

7-Acetylamino-8-chloroisoquinoline

A solution of 7-aminoisoquinoline (1 gm.) in glacial acetic acid (10 cc.) and acetic anhydride (5 cc.) was heated on the steam bath for one-half hour and then cooled to 20° C. Sodium acetate (1 gm.) was added and chlorine gas was passed in slowly with cooling until 0.7 gm. was absorbed. The solvent was removed from the reaction mixture under reduced pressure, the residue dissolved in dilute hydrochloric acid, and the solution basified with ammonium hydroxide. The precipitate was filtered, washed, dried, and crystallized twice from benzene; light-yellow prisms, m.p. 166° to 167° C.; yield, 0.7 gm. Calc. for $C_{11}H_9ON_2Cl$: C, 59.87; H, 4.08; N, 12.70%. Found: C, 59.90, 59.97; H, 4.43, 3.62; N, 12.81, 12.99%.

In a few other experiments the chlorinated product was a mixture which could not be purified by crystallization from benzene.

7-Amino-8-chloroisoquinoline

7-Acetylamino-8-chloroisoquinoline (0.5 gm.) was dissolved in 20% hydrochloric acid (10 cc.) and the solution heated under reflux for one-half hour. The cooled solution was basified with dilute ammonium hydroxide and the precipitate, filtered, washed, and dried; yield 0.40 gm.; crystallized from benzene, fine white needles, m.p. 177° to 179° C. Calc. for $C_9H_7N_2Cl$: C, 60.50; H, 3.92; N, 15.69%. Found: C, 60.30, 60.15; H, 3.84, 3.99; N, 15.43%. This compound when deaminated with hypophosphorous acid yielded a compound melting at 55° to 56° C. either alone or in admixture with 8-chloroisoquinoline (3). Also, when diazotized and then reduced with stannous chloride it yielded golden-yellow needles which melted at 173° to 174° C. (with decomposition) alone or in admixture with 7-hydrazino-8-chloroisoquinoline (XI).

7-Hydroxy-8-chloroisoquinoline

. A solution of 2-chloro-3-hydroxybenzaldehyde (2) (15 gm.) and aminoacetal (15 gm.) was heated on the steam bath for one-half hour, and then the water of reaction removed by alternate addition and distillation of benzene. To the cooled, well dried, dark brown residual liquid was added with stirring and cooling 76% sulphuric acid (100 cc.) previously cooled to 0° C. After stirring the reaction mixture for four hours at 2° to 5° C., it was allowed to stand for 40 hr. at 8° C. and 30 hr. at room temperature. The resulting thin slurry was dissolved by addition of water, basified with ammonium hydroxide, and buffered with sodium carbonate. The precipitated brown solid was filtered and sublimed at 175° C. (1 mm.). The yield of white sublimate was 12.0 gm. or 64%; crystallized from methanol, white needles, m.p. 230° to 231° C. Calc. for C_9H_8NOCl : C, 60.16; H, 3.34; N, 7.80%. Found: C, 59.87, 60.17; H, 3.67, 3.53; N, 7.37%.

The Bucherer Reaction with 7-Hydroxy-8-chloroisoquinoline

Into a suspension of 7-hydroxy-8-chloroisoquinoline (0.5 gm.), water (8 cc.), and concentrated ammonium hydroxide (3 cc.) was passed sulphur dioxide until 2.5 gm. was absorbed. To the resulting solution, concentrated ammonium hydroxide (20 cc.) was added and the reaction mixture heated at 120° C. for 16 hr. in a hydrogenation bomb. The amber solution was taken to dryness under reduced pressure, and the residue heated with concentrated hydrochloric acid in order to drive off most of the sulphur dioxide and then basified with sodium hydroxide and cooled. The precipitated solid (0.07 gm.) when crystallized from benzene melted at 203° to 204° C. alone or in admixture with 7-aminoisoquinoline.

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REFRACTIVE INDEX OF HYDROGEN PEROXIDE SOLUTIONS. A REVISION¹

BY PAUL A. GIGUÈRE AND PIERRE GEOFFRION²

Abstract

Values for the refractive index of aqueous solutions of hydrogen peroxide reported some years ago by the senior author have been found in error by more than the estimated accuracy of measurements. The error is proportional to the concentration of the solutions and amounts to about 5×10^{-4} for the pure peroxide. More accurate data have now been obtained by using an instrument of higher precision and by refining the analytical method. In addition, some anhydrous hydrogen peroxide has been prepared; its refractive index at 25° C. was $1.4067_1 \pm 0.0001$ with an average temperature coefficient of 3.4×10^{-6} per degree.

A few years ago the refractive index of hydrogen peroxide solutions was determined in this laboratory (2) in order to provide a convenient method of instrumental analysis. The measurements, made with a Pulfrich refractometer, covered the whole concentration range in steps of 10% at four different temperatures; the solutions were analyzed by the usual titration with potassium permanganate. At that time the results were believed correct to about 1 part in 1000. However, a series of measurements made recently in another laboratory (5) have revealed more serious discrepancies. A review of the question has led to the following conclusions. The error could be traced either to the instrument or to the analysis of solutions or both. The refractometer itself could not be suspected since it was repeatedly checked with distilled water throughout the investigation. On the other hand the temperature was not controlled with enough accuracy, as has been discovered since. The practice of not using the metal water jacket in order to avoid decomposition of the peroxide resulted in a liquid sample that was slightly warmer or cooler than the prism, depending on whether the measurements were made below or above room temperature. Since the temperature coefficient of the refractivity of hydrogen peroxide is three times as large as that of water the ensuing error increased with the concentration of solutions. Still this could not very likely be the only source of error as it would imply deviations of the order of 2° C.

The chemical analysis is equally open to question; besides it is not so easily checked against an absolute method. (The results of Huckaba and Keyes (3) were not yet available when the present investigation was completed.) Provided the reaction is quantitative, volumetric methods, when properly carried out, are capable of an accuracy of the order of 1 part in 1000. This is entirely satisfactory for the more dilute solutions, but as the concentration

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of hydrogen peroxide is increased the absolute error increases accordingly. The same is true, indeed, of all determinations in which the major constituent is found directly. Titration with standard potassium permanganate was considered the most reliable; necessary precautions were always taken to prevent any appreciable decomposition of the peroxide due to formation of manganese dioxide. Standardization of the permanganate had been carried out according to the older method. This time the procedure recommended by Fowler and Bright (1) was followed. In fact the two methods were compared and a difference of the order of 0.15% was found.

Experimental

To minimize these errors the new measurements were made as follows. A Precision Abbé refractometer (Bausch and Lomb) being available in this laboratory, it was used in preference to the Pulfrich type because of its higher accuracy (2 to 3×10^{-5}). It was calibrated by means of a glass test piece supplied by the maker. The temperature was read to 0.1°C . on a thermometer placed next to the prisms; water was circulated from a thermostat controlled to $\pm 0.02^{\circ}\text{C}$. The cement holding the prisms had to be covered with Ceresin wax to prevent decomposition of hydrogen peroxide. A special feature of the instrument proved very useful for this work; an auxiliary lens is provided which can be moved into the telescope to give a view of the liquid layer between the prisms. Thus any appreciable decomposition could be detected from the presence of oxygen bubbles. Solutions that were too unstable were rejected. The determinations were made at 25° and 20°C . with the sodium light.

The solutions used were obtained by distillation of Becco's 90% hydrogen peroxide. In the lower concentration range it was necessary to dilute them with redistilled water; as a result they invariably showed a marked tendency to decompose, so that a trace of inhibitor (sodium stannate) had to be added. The stabilizing effect became noticeable only after a certain time (30 to 60 min.). Improvements in the analytical technique consisted mainly in using larger volumes of reagents, 90 to 95 cc. and a better standardization method. Duplicate analyses generally agreed among themselves to 1 part in 1000 or better. A special series of determinations were carried out to compare the accuracy of the permanganate and the thiosulphate methods. Samples of about 0.25 gm. of a 95% hydrogen peroxide solution in tiny vials were weighed to 0.01 mgm. on a microanalytical balance, using a set of certified weights. The vials were dropped into 500 cc. Erlenmeyer flasks containing 150 cc. of redistilled water and 3 cc. of sulphuric acid, and the titrations run immediately with freshly standardized reagents. The same burette, 100 cc. certified Normax, calibrated in 0.1 cc., was used for all titrations. The end points were estimated to ± 0.02 cc. after allowing reasonable time for draining.

The potassium permanganate solution, about 0.15 *N*, was standardized against certified sodium oxalate (National Bureau of Standards), and according to the above mentioned method (1). The sodium thiosulphate was standardized against the permanganate for comparison purpose. For peroxide analyses the acetic acid - ammonium molybdate method was followed with the latter reagent. All operations were done the same day; the temperature of the various solutions did not vary by more than one degree. As may be seen from the results of this test (Table I) the permanganate method is somewhat superior to the thiosulphate one.

TABLE I
ANALYSIS OF A CONCENTRATED HYDROGEN PEROXIDE SOLUTION

n_D (25° C.)	Permanganate method		Thiosulphate method	
	Normality	Wt. % H ₂ O ₂	Normality	Wt. % H ₂ O ₂
1.40213	0.1484 ₈	94.56 ₇	0.1497 ₉	94.62 ₄
1.40211	0.1486 ₈	94.53 ₈	0.1497 ₉	94.52
1.40211	0.1485 ₈	94.60 ₄	0.1498 ₈	94.58
1.40209	0.1486 ₁		0.1498 ₈	94.46 ₈
1.40212	0.1484 ₈		0.1497 ₇	
1.40211	0.1485 ₈			
1.40211	0.1485 ₈	94.57	0.1498 ₁	94.55
±0.00002	±0.0001	±0.03	±0.00005	±0.08

Since the accuracy of the chemical analysis was the limiting factor in the present work an attempt was made to prepare some pure anhydrous hydrogen peroxide. Four liters of a 90% commercial solution was distilled under a pressure of 3 to 4 mm. of mercury in an all-glass apparatus connected with ground glass joints; the 3 ft. rectifying column was filled with glass rings. Thus a 99.8% solution was obtained (about one-half liter) which was then subjected to fractional crystallization after the technique outlined by Maass and Hatcher (4). The progress of concentration was followed by measuring the refractive index with an immersion refractometer. After the second operation this property did not change further; the observed value, 1.4067₂ at 25° C., is estimated to be correct to ±0.0001, considering the difficulty of removing last traces of water. The average temperature coefficient between 15 and 25° C. was 3.4×10^{-5} per degree.

Results

The experimental data listed in Table II were plotted on a large graph, one division corresponding to 0.1% for composition and 0.0001 for refractive index. All points fell closely on a smooth line, indicating that the measurements were self-consistent. Values extrapolated from the first published data at 20° and 24° C. were also plotted on the same graph for comparison. The

TABLE II

REFRACTIVE INDEX OF HYDROGEN PEROXIDE SOLUTIONS MEASURED AT 20 AND 25° C. WITH THE SODIUM-D LINE

%H ₂ O ₂	n _D		%H ₂ O ₂	n _D	
	25° C.	20° C.		25° C.	20° C.
0.00	1.3325 ₁	1.3329 ₉	60.6 ₈	1.3738 ₉	1.3750 ₈
10.1 ₀	1.3388 ₁	1.3394 ₈	70.1 ₈	1.3815 ₁	1.3828 ₄
19.9 ₈	1.3452 ₁	1.3460 ₃	79.8 ₈	1.3892 ₇	1.3907 ₂
30.1 ₁	1.3520 ₈	1.3529 ₈	92.3 ₈	1.3999 ₈	1.4015 ₇
40.0 ₈	1.3588 ₈	1.3598 ₈	96.2 ₈	1.4033 ₃	1.4049 ₈
50.1 ₀	1.3661 ₁	1.3672 ₄	99.3 ₀	1.4060 ₇	1.4077 ₄

two sets agree exactly up to about 40% where a slight deviation begins to be noticeable at that scale. From that concentration up, the difference increases steadily, the present indices being lower. The data of Table III, obtained

TABLE III

REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 25° C.

H ₂ O ₂ %		0.0	0.2	0.4	0.6	0.8	H ₂ O ₂ %		0.0	0.2	0.4	0.6	0.8
0	1.3	325	326	327	328	329	33	1.3	540	541	543	544	546
1		331	333	334	335	336	34		547	548	550	551	553
2		338	339	340	341	343	35		554	555	557	558	560
3		344	345	347	348	349	36		561	562	564	565	567
4		350	352	353	354	355	37		568	569	571	572	574
5		357	358	359	360	362	38		575	576	578	579	581
6		363	364	365	367	368	39		582	583	585	586	588
7		369	370	372	373	374	40		589	590	592	593	595
8		376	377	378	379	381	41		596	598	599	600	602
9		382	383	384	386	387	42		603	605	606	608	609
10	1.3	388	389	391	392	393	43	1.3	611	612	613	615	616
11		395	396	397	398	400	44		618	619	621	622	623
12		401	402	404	405	406	45		625	626	628	629	631
13		407	409	410	411	412	46		632	633	635	636	638
14		414	415	416	418	419	47		639	641	642	643	645
15		420	421	423	424	425	48		646	648	649	651	652
16		427	428	429	430	432	49		653	655	656	658	659
17		433	434	436	437	438	50		661	662	663	665	666
18		439	441	442	443	444	51		668	669	671	672	674
19		446	447	448	450	451	52		675	677	678	680	681
20	1.3	452	453	455	457	458	53	1.3	683	684	686	687	688
21		459	460	462	463	464	54		690	691	693	694	696
22		466	467	468	470	471	55		698	699	700	702	703
23		472	474	475	476	478	56		705	706	707	709	711
24		479	480	482	483	484	57		712	713	715	716	718
25		486	487	488	490	491	58		719	721	722	724	725
26		492	494	495	496	498	59		727	728	730	731	733
27		499	500	502	503	504	60		734	736	737	739	740
28		506	507	508	510	511	61		742	744	745	747	748
29		512	514	515	516	518	62		750	752	753	755	756
30	1.3	519	520	522	523	525	63	1.3	758	760	761	763	764
31		526	527	529	530	532	64		766	768	769	771	772
32		533	534	536	537	539	65		774	776	777	779	780

TABLE III—*Concluded*REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 25° C.—*Concluded*

H ₂ O ₂ %		0.0	0.2	0.4	0.6	0.8	H ₂ O ₂ %		0.0	0.2	0.4	0.6	0.8
66		782	784	785	787	788	84		928	930	932	933	935
67		790	792	793	795	796	85		937	939	940	942	944
68		798	800	801	803	804	86		945	947	949	950	952
69		806	808	809	811	812	87		954	956	957	959	961
70		814	816	817	819	820	88		962	964	966	968	969
71		822	824	825	827	828	89		971	973	974	976	978
72		830	832	833	835	836	90		880	981	983	985	986
73		838	840	841	843	844	91		988	990	992	993	995
74		846	848	849	851	852	92		997	999	*000	*002	*004
75		854	856	857	859	860	93	1.4	006	007	009	011	013
76	1.3	862	864	865	867	868	94		014	016	018	020	021
77		870	872	873	875	876	95		023	025	027	028	030
78		878	880	881	883	884	96		032	034	035	037	039
79		886	888	889	891	892	97		041	042	044	046	048
80		894	896	897	899	901	98		049	051	053	055	056
81		903	904	906	908	909	99		058	060	062	063	065
82		911	913	915	916	918	100	1.4	067				
83		920	921	923	925	927							

from this large plot, show that extrapolation to 100% gives the same value as the direct determination with the immersion refractometer. The correction factors for temperature given in Table IV supersede those previously published.

TABLE IV

TEMPERATURE CORRECTIONS TO BE SUBTRACTED FROM THE PERCENTAGE OF HYDROGEN PEROXIDE (IN TABLE III)

Temp., °C.	Approximate concentration									
	10	20	30	40	50	60	70	80	90	100
20	0.9	1.2	1.3	1.4	1.4	1.5	1.6	1.7	1.8	1.9
21	0.8	0.9	1.0	1.1	1.1	1.2	1.2	1.3	1.4	1.5
22	0.6	0.7	0.8	0.9	0.9	1.0	1.0	1.0	1.1	1.1
23	0.4	0.4	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.8
24	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4

Refractive index measurements offer a most convenient method of determining the concentration of hydrogen peroxide solutions. Of the various types of instruments available the immersion refractometer is the best adapted to this purpose because of its high accuracy and good temperature control; in addition the solutions come in contact only with the glass prism. Two prisms (*A* and *B*) cover nearly all the concentration range. The Precision Abbé is also very accurate and easily thermostatically controlled. As mentioned above, some precautions are necessary to prevent decomposition of the peroxide on the cement; the chromium plated metal parts do not seem to

be affected by it. The Pulfrich refractometer is satisfactory for measurements around room temperature. Whatever the type of instrument used, the measurements must be made as soon as thermal equilibrium permits, to prevent appreciable change in composition of the solutions due either to evaporation or to the hygroscopic nature of the more concentrated ones (above 90%). Also, the solutions must be very stable, as any decomposition causes a blurred image of the dividing line owing to light scattering by gas bubbles.

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NOTES

The Cobalt Chloride Method for Determining Bound Water*

In the course of another investigation, a method was desired for determining the extent of solvation of methyl cellulose in aqueous solutions. In an article describing a promising method, Hatschek (4) stated: "When gelatin gels containing cobaltous chloride are allowed to dry at temperatures from 15° to 30°, they turn a pure blue before all the water which they can lose at the latter temperature has evaporated. The water still remaining in the gel must therefore be considered as water bound by the gelatin in the sense that it is no longer free to hydrate the cobaltous chloride". Hatschek made up disks of gelatin containing slightly over 20% of cobaltous chloride (on a dry basis) and visually followed the color change from red through purple to blue as they dried. The disks that had just turned blue were weighed and then the remaining moisture was removed by drying to constant weight at 100° C. The loss in weight was taken to represent the "bound water", which was determined to be 0.43 to 0.51 gm. per gm. dry gelatin for various gelatins. This agreed well with the value obtained by Moran (7) using a different method.

In the present investigation, the method of Hatschek (4) was applied to "gels" of methyl cellulose (Dow methocel, 15 cps.), using the suggested concentration of about 20% cobaltous chloride (Merck's reagent grade). A second experiment, in which a low concentration of cobaltous chloride was used, resulted in a much lower value for the "bound water". For this reason a series of measurements were made with varying concentrations of cobaltous chloride. The results are shown in Fig. 1, upper curve.

An extension of the measurements to gelatin showed that variations in the cobaltous chloride concentration affected the results in a similar manner. Dried Eastman pigskin gelatin was used. The results are given in the lower curve of Fig. 1. Points calculated from Hatschek's data (4) and those of Weidinger and Pelsner (8) are included.

These latter investigators considered their values at different concentrations to be fairly constant and to agree with the value at the break point in the curve relating side chain spacings (from X-ray data) to amount of adsorbed water. This break occurred at about 0.45 gm. water per gm. dry gelatin. These authors also compared the adsorption isotherm of water on pure gelatin with that of water on gelatin containing about 2% cobaltous chloride. The isotherms were very similar up to a relative vapor pressure of slightly over 0.8, after which they began to separate and the color changed in the sample containing cobaltous chloride. This point corresponded to about 0.3 gm. water

* Issued as Report No. 20.

per gm. dry gelatin. These isotherms were obtained by exposing the samples, over sulphuric acid solutions in a desiccator, equilibrium being attained in about four weeks.

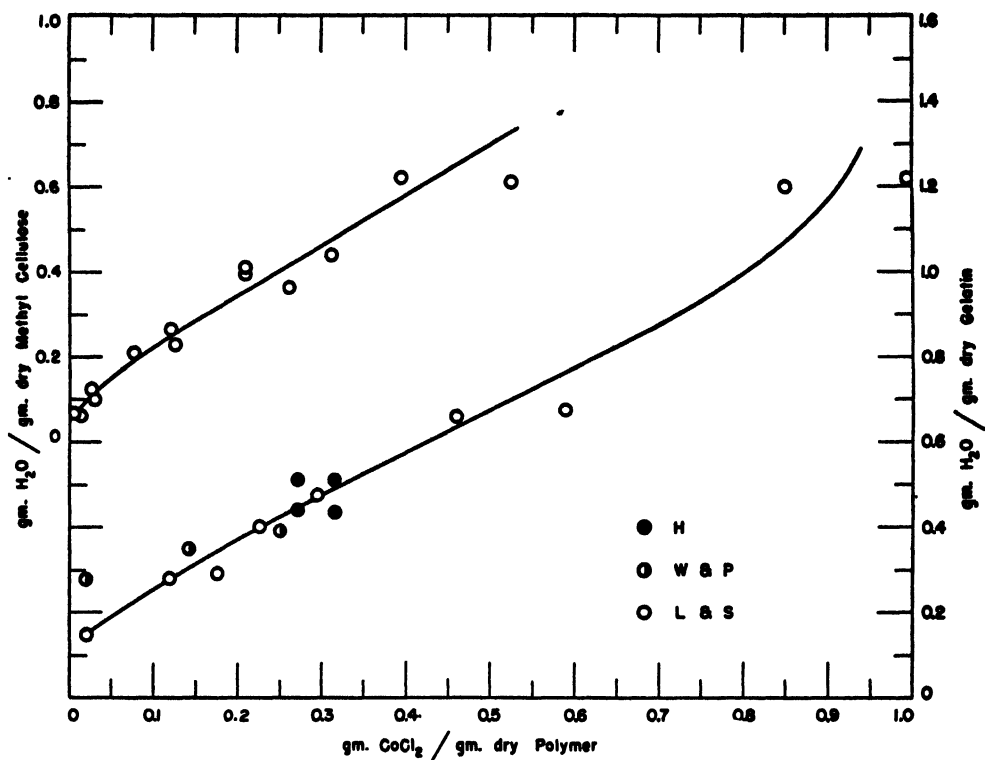


FIG. 1. Water content of polymer at the color change (purple to blue) plotted against cobaltous chloride concentration. H—Hatschek (4), W and P—Weidinger and Pelsler (8), L and S—this investigation.

To check the significance of the point of separation of the isotherms, water-gelatin isotherms were obtained in this investigation, using the more accurate isopiestic method (5), in which equilibrium with sulphuric acid solutions was attainable in two days at 30° C. It was found that the isotherms were separated over their entire length, the amount of separation increasing with concentration of cobaltous chloride and with increasing relative vapor pressure. Concentrations of cobaltous chloride in the gelatin disks were 0, 0.3, 3.3, 12, 20, and 30%. At a relative pressure of 0.5 the weight of water adsorbed per gram dry gelatin for each of these concentrations was 0.15, 0.16, 0.17, 0.22, 0.30, and 0.51 gm., respectively, while at a relative pressure of 0.82 the corresponding values were 0.24, 0.25, 0.29, 0.46, 0.67, and 1.20 gm.

Since the color in the gelatin disks containing low concentrations of cobaltous chloride was quite faint, the color changes were difficult to judge accurately by eye. It was therefore decided to carry out some experiments on dilute solutions of cobaltous chloride in dry solvents to which water could be added and the color changes determined accurately by means of a colorimeter.

Dried reagent acetone and absolute ethyl alcohol were used as solvents. To 5 cc. of the blue solutions of cobaltous chloride, water was added from a graduated pipette in small increments, colorimeter readings being taken after each addition. A 6000 Å filter was used so that the light was strongly absorbed when the solutions were blue and a sharp increase in transmission occurred as soon as the red coloration began to appear. The weight of water per gram of dry solvent at this point is shown plotted against cobaltous chloride concentration in Fig. 2.

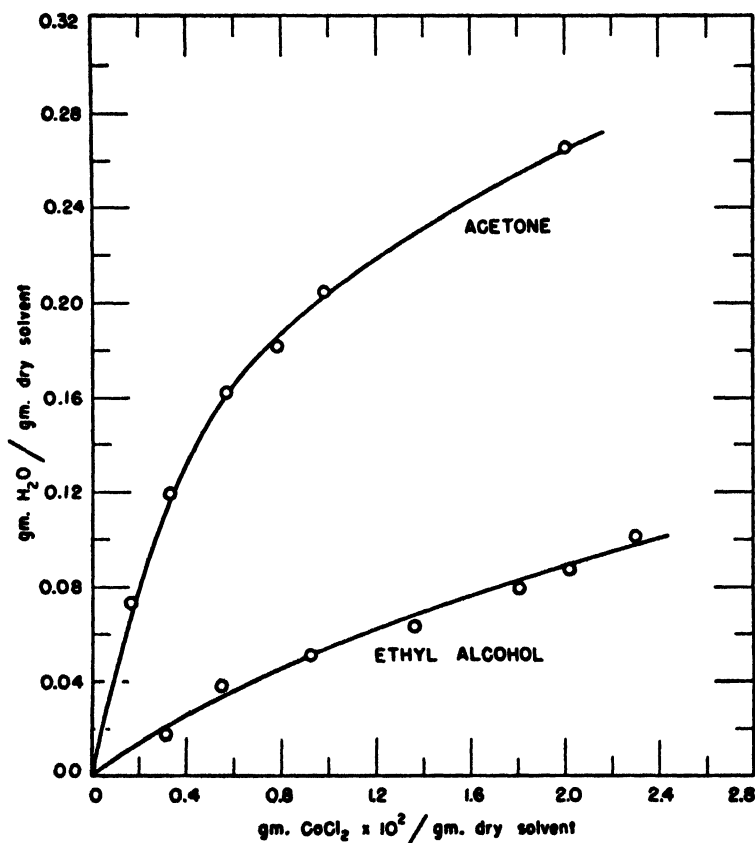


FIG. 2. Water content of solvent at the color change plotted against cobaltous chloride concentration.

The solvent - cobaltous chloride systems cannot be considered on exactly the same basis as the gelatin - cobaltous chloride system, since the cobaltous chloride is thought to be held intermicellarly in the latter (8). However, water which is strongly bound by the solvent would not be expected to cause a color change in the cobaltous chloride. The curves obtained are similar in type to those for gelatin and methyl cellulose in that they extrapolate to zero and rise rapidly with increasing cobaltous chloride concentration. There is no reason to believe that any one point on any of these curves gives a more meaningful value for the "bound water" than any other.

Although it is commonly thought that the color changes in cobaltous chloride are due to hydration, Donnan and Bassett (3) and Bassett and Croucher (1) have shown that hydration processes may be associated with the color changes though not themselves responsible for them and that, in some cases, water is not at all essential. To illustrate the latter point, solid anhydrous cobaltous chloride and solutions of cobaltous chloride in dry ethyl alcohol are blue at ordinary temperatures, but turn red at very low temperatures. According to these authors the blue color is due to the complex anions, CoCl_4^{--} or $[\text{CoCl}_3, \text{H}_2\text{O}]^-$, and the red color is due to the cations, Co^{++} , $\text{Co}(\text{H}_2\text{O})_6^{++}$, $\text{Co}(\text{H}_2\text{O})_4^{++}$, $\text{Co}_2(\text{H}_2\text{O})_{10}^{++++}$, or $\text{Co}_2(\text{H}_2\text{O})_6^{++++}$, any of which may predominate, depending on concentration and temperature. Bassett and Croucher (1) suggest that a slight interchange of electronic linkages even in the solid crystals may introduce ions that impart the slight purplish tinge to the hexahydrate. Aqueous solutions of cobaltous chloride may be red, violet or blue, depending on concentration and temperature.

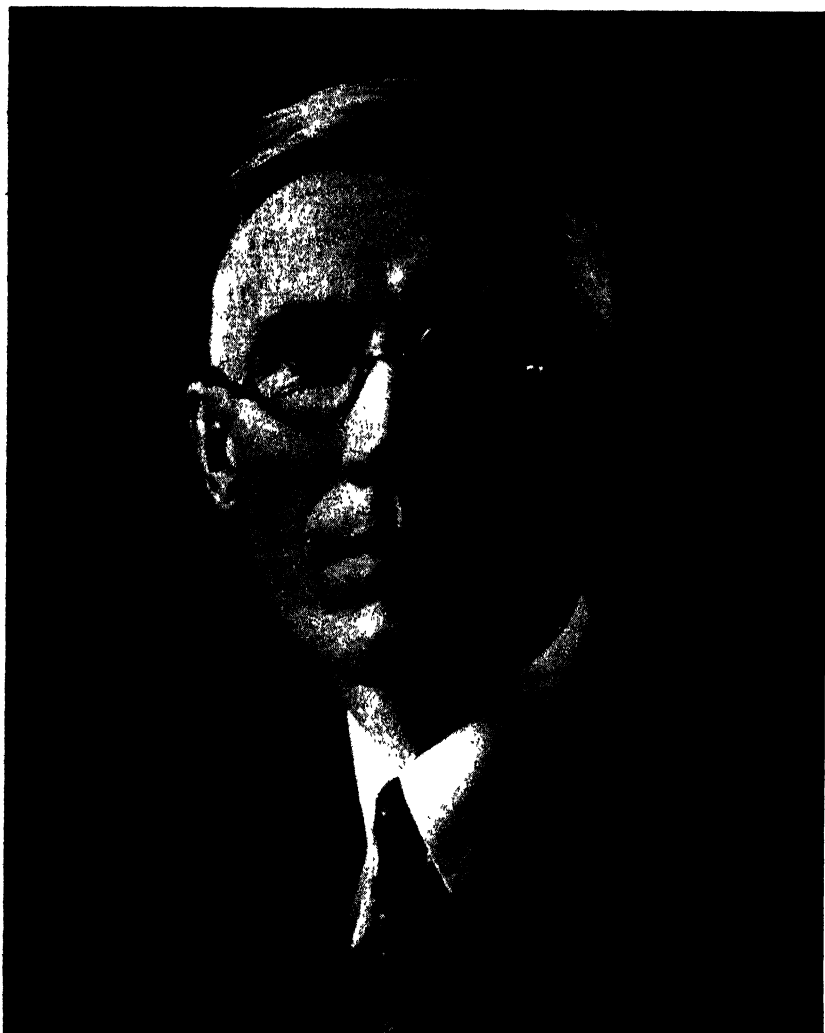
To further complicate the picture, it has been shown (2, 6) that alcoholates and acetates of cobaltous chloride exist. It is rather likely, therefore, that some type of combination occurs between cobaltous chloride and the polar groups of gelatin and methyl cellulose. The extent of combination would probably be dependent on concentration.

In view of these facts, it is not surprising that the values of the "bound water" determined by the cobalt chloride method varied so markedly with concentration. It must be concluded that this method cannot give a meaningful value for bound water.

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DAPHNE LINE
H. SHEFFER



Photograph by Notman.

J. J. Herwaldson

To

PROFESSOR T. THORVALDSON
this issue is dedicated by his
friends and students as a tribute
on the occasion of his retirement
as Director of the Chemistry
Department at the University
of Saskatchewan

Dr. Thorbergur Thorvaldson

Thorbergur Thorvaldson was born in Iceland but came to Canada as a child with his parents who settled on the west shore of Lake Winnipeg in the neighborhood of Gimli. He attended public and high school in Manitoba and then entered Wesley College (University of Manitoba) where he took the Arts course with chemistry as his special subject.

After graduation with honors he proceeded to Harvard University for graduate study and came under the direction of T. W. Richards and G. P. Baxter, two of America's most distinguished chemists whose influence shaped Thorvaldson's scientific outlook in no small measure. His studies in thermochemistry and atomic weight determination in the Harvard laboratories gave him those ideals of accuracy and thoroughness that are part of the Harvard chemical tradition and which have been conspicuous in his own researches all through his subsequent career. He received his doctorate in 1911 and was awarded a traveling fellowship which enabled him to spend a year at the University of Liverpool under F. G. Donnan working on problems of electrochemistry, and a year in Germany mostly at Dresden studying photochemistry with R. Luther.

After his return to America he spent another year at Harvard in teaching and research and then in 1914 was appointed Assistant Professor of Chemistry at the University of Saskatchewan. Here he began the teaching of quantitative analysis and physical chemistry which he has carried on with such distinction through the following years. In 1919 he became head of the Chemistry Department and has directed the work of the department with such outstanding skill and good judgment that it is now and has been for some years one of the strongest departments in the university.

In the 20's he began his researches on the chemistry of cement with especial reference to the action of sulphate waters on concrete, and the methods of increasing the resistance of cement to chemical attack. His fundamental work on the preparation and physicochemical properties of the pure components of cement has brought him international recognition. He was elected a Fellow of the Royal Society of Canada in 1926. The Government of Iceland, a few years ago, conferred on him a Knighthood of the Order of the Falcon, and his alma mater, the University of Manitoba, more recently awarded him the degree of Doctor of Science, *honoris causa*.

Dr. Thorvaldson's personal qualities, his geniality, his sense of fairness, and his sympathetic understanding of human relationships have been a constant inspiration to his students and colleagues and have created in his department a remarkable atmosphere of good will. His retirement from both the chair of chemistry and the deanship of the College of Graduate Studies is deeply regretted but he goes with the best wishes of his hosts of friends for many years of leisurely activity in the studies which he still plans to pursue.

S. BASTERFIELD

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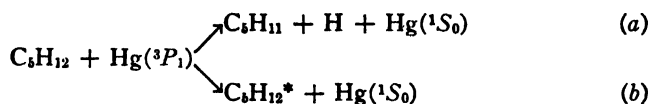
NUMBER 4

THE MERCURY PHOTSENSITIZED REACTIONS OF NEOPENTANE¹

BY B. DEB. DARWENT AND E. W. R. STEACIE

Abstract

The mercury photosensitized reactions of neopentane have been investigated at pressures between 50 and 400 mm. of mercury and between 25° and 200° C., in the presence and absence of hydrogen. The products are largely hydrogen and dineopentyl. The quantum yield of hydrogen production is 0.004 at room temperature and has a positive temperature coefficient corresponding to $E = 4.3$ kcal. mole⁻¹. The facts are consistent with the reactions:—



as the initial step. The majority of the reaction goes by (b), and the active molecules produced, $\text{C}_5\text{H}_{12}^*$, are nearly all deactivated.

Introduction

The only bond broken in the initial act of the mercury photosensitized reactions of the lower paraffin hydrocarbons is that between carbon and hydrogen atoms. The C-H bonds in neopentane are almost identical with those in ethane; however, the neopentane molecule is much more symmetrical than ethane and so resembles methane more closely. It has recently been shown (3) that the initial step in the reaction between ethane and $\text{Hg}({}^3\text{P}_1)$ atoms, the breaking of a C-H bond, is probably about 100% efficient and that at very high pressures the quantum yield of hydrogen production approaches the theoretical value of unity. On the other hand Morikawa, Benedict, and Taylor (5) found that the quantum yield in the similar reaction of methane was only 0.08 at 20° C., and had an activation energy of about 4.5 kcal. mole⁻¹. If the efficiency of these reactions depends primarily on the strength of the bond being broken, neopentane would be expected to react, like ethane, with a reasonably high quantum yield. If, however, the symmetry of the molecule plays an important part it is likely that neopentane would behave more like methane. Hence the investigation of the mercury photosensitized reactions of neopentane may give some information about the relative importance of bond strength and symmetry in these reactions.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1897.

Experimental

Neopentane was prepared by the Grignard reaction between tertiary butyl chloride and methylmagnesium chloride*. The product was washed with sulphuric acid, subjected to photobromination and fractionated to remove dibromides. The final purification to remove paraffinic impurities (chiefly dimethylbutanes) was accomplished by exhaustive photosensitization (4) followed by a second fractional distillation. The fraction used was found to be at least 99.8% pure by mass spectrometer analysis. Hydrogen was taken from a cylinder of electrolytic gas and purified by passage through a hot palladium tube.

The reaction system was of conventional design in which the gas was circulated through a mercury saturator, desaturator (20° C.), and a cylindrical quartz reaction vessel enclosed in a tubular furnace. Mercury cutoffs were used to isolate the reaction system from the storage and analytical portions of the apparatus. The total volume of the reaction system was 345 cc., the quartz reaction vessel 244 cc., and the circulation rate about 200 cm.³ min.⁻¹ at the pressure prevailing in the apparatus. The temperature was controlled manually to within $\pm 1^\circ$ C. and was measured by a calibrated copper-constantan thermocouple in the annular space between the outer wall of the reaction vessel and the inner wall of furnace.

Unreversed $\lambda 2537$ was obtained from a low pressure mercury lamp with neon (3 mm.) as carrier gas. The intensity, very nearly all of which is due to $\lambda 2537$, was measured by the rate of hydrolysis of monochloroacetic acid (0.5 *N*) using published values (7) for the quantum yield of the hydrolysis and applying a small blank correction for the dark reaction. The quantum input was found to be 1.1×10^{-5} einstein hr.⁻¹.

The products boiling below neopentane were analyzed and measured in a modified (6) version of the Ward fractionation apparatus (9). The results of these analyses showed that the products boiling below neopentane consisted almost entirely of hydrogen with smaller amounts of methane; only traces of C₂, C₃, and C₄ hydrocarbons were found in the experiments at 25° C. and, in the majority of these experiments, the analysis was simplified to the determination of the volume and composition of the H₂-CH₄ fraction. At higher temperatures C₂ and C₃ hydrocarbons were present in increasing amounts but under all conditions hydrogen was by far the most important of the lighter products.

In addition to the low boiling products a heavy oily substance was also produced. To investigate the nature of this substance a comparatively large amount of neopentane was introduced and condensed in a trap cooled to a temperature such that the neopentane was mainly in the liquid state with a vapor pressure of about 150 mm. The vapor was circulated at room temperature through an annular quartz cell which provided a much larger incident surface. The experiment was interrupted periodically and the noncondensable gas pumped off from a trap in liquid air. The properties of the liquid product so obtained are compared with those of dineopentyl in Table I, and it is evident that this product must consist very largely of dineopentyl.

* We are indebted to Dr. A. Cambron and Mr. R. A. Bannard for this preparation.

TABLE I

NATURE OF THE HEAVY PRODUCT OF THE MERCURY PHOTSENSITIZED REACTION OF NEOPENTANE

	B.p., °C.	Density	n_D^{20}
Product	136 - 137	0.718	1.4060
Dineopentyl	136.8	0.7179	1.4053

Results

The effects of time and pressure on the rate of production of noncondensable gases at 25° C. are shown in Figs. 1 and 2. It is evident that the reaction rate is very low in the early stages of the experiment and that it increases

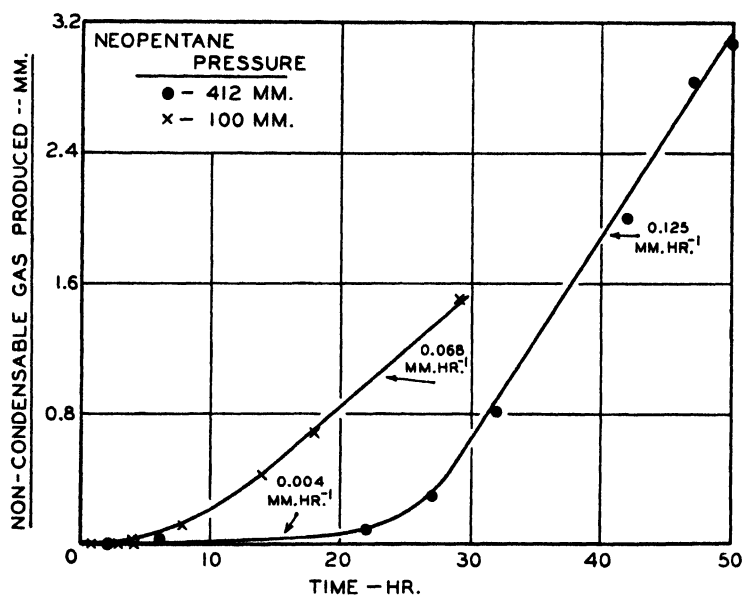


FIG. 1. The production of noncondensable gas at 25° C. The results are expressed as millimeters per hour in the reaction volume.

with time to a much higher, and approximately constant, value. The fact that the neopentane pressure does not affect the initial rate but that the "induction period" decreases with decreasing pressure is shown clearly in Fig. 2. These experiments were carried out by stopping the reaction at frequent intervals, freezing out the condensable products in liquid air, and measuring the pressure of the noncondensable gases with a McLeod gauge. This procedure enabled the reaction to be followed from very small conversions and gave a reasonably accurate measure of the initial rate.

The marked acceleration of the reaction in the later stages could have been due to the accumulation of hydrogen and/or dineopentyl. That the rate is greatly accelerated by the addition of small amounts of hydrogen is shown by the results given in Table II.

The rate (0.06 to 0.07 mm. hr.⁻¹) in the presence of added hydrogen is identical with that found in the later stages of the reaction at 100 mm. (see Fig. 1), so that the accumulation of hydrogen in the reaction is, at least partly,

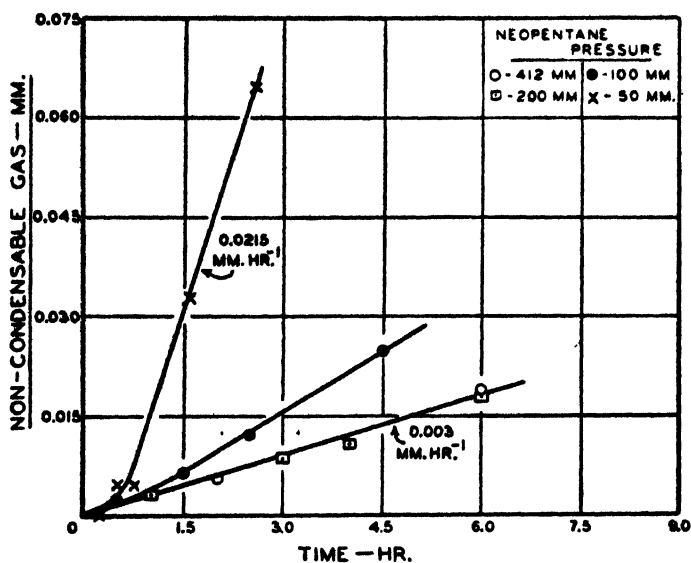


FIG. 2. The production of noncondensable gas in the initial stages of the reaction at 25°C .

TABLE II

THE EFFECT OF ADDED HYDROGEN ON THE RATE

Neopentane pressure = 100 mm. Reaction temp. = 25°C .

P_{H_2} , mm.	0.000	1.00	2.00	12.8
Rate, mm. hr. ⁻¹	0.003	0.07	0.06	0.07

responsible for the increased rate. However, experiments in which the reaction was stopped at a point where the rate had already increased, the noncondensable gases pumped off from liquid air, and the reaction allowed to proceed, showed that the rate of production of noncondensable gases in the second portion was equal to the final rate in the first portion of the experiment, indicating that dineopentyl also was responsible for accelerating the rate.

The rate of formation of methane at 25°C . was found to increase with decreasing neopentane pressure, thus the noncondensable gases contained 10.9% CH_4 at 103.3 mm. and only 3.8% CH_4 when the neopentane pressure was increased to 412.3 mm. Hence the production of methane from neopentane depends on the pressure of the hydrocarbon in much the same way as in the similar reactions of ethane (3) and propane (2).

The effect of temperature on the reaction was studied using a technique similar to that described above. The results obtained are given in Figs. 3 and 4 and in Table III.

TABLE III
EFFECT OF TEMPERATURE ON INITIAL RATE
Neopentane pressure = 100 mm.

Temp., °C.	Noncondensables		Hydrogen		Methane	
	Rate, mm.hr. ⁻¹ × 10 ³	% CH ₄	Rate, mm.hr. ⁻¹ × 10 ³	φ _{H₂}	Rate, mm.hr. ⁻¹ × 10 ³	φ _{CH₄}
25	3.0	11	2.7	0.0045	0.3	0.00055
100	11.0	13	9.6	0.0167	1.4	0.0025
200	44.0	16	37.0	0.0675	7.0	0.0128

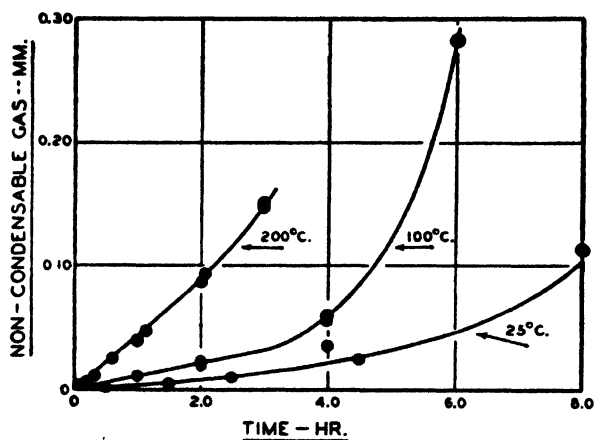


FIG. 3. The effect of temperature on the production of noncondensable gas. Neopentane pressure = 100 mm.

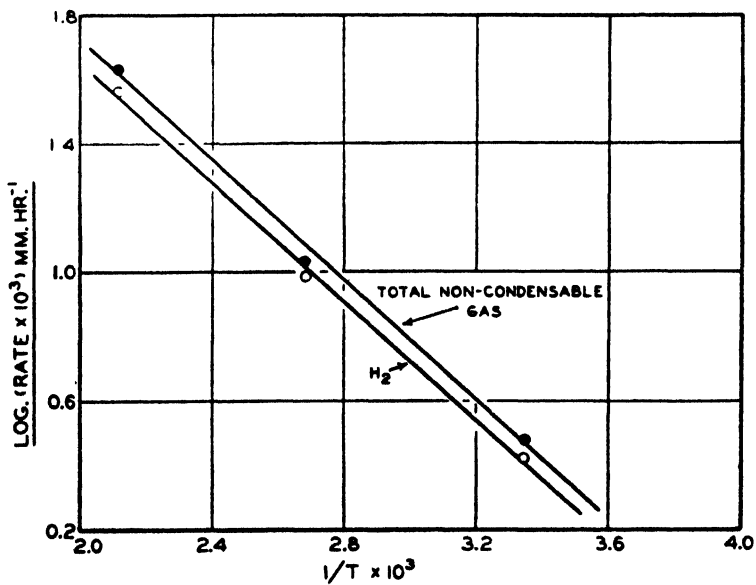


FIG. 4. The temperature coefficient.

In Table III the rates are initial values, expressed in $\text{mm. hr.}^{-1} \times 10^3$, and have, in all cases, been corrected to allow for the temperature of the reaction vessel. The values are the averages of two or three concordant experiments. It is significant that these results were obtained from experiments of different lengths, showing that the composition of the noncondensable gases does not vary greatly with the extent of the reaction as found with ethane (3). The activation energies for the production of hydrogen and methane ($E_{\text{H}_2} = 4.3$ and $E_{\text{CH}_4} = 5.1$ kcal. per mole) were obtained from these results, in the usual way (Fig. 4).

It was found that C_2 and C_3 hydrocarbons were present in increasing amounts at higher temperatures. The rates of production of those substances were almost identical with that of methane at 100°C . No C_4 hydrocarbons were detected at any temperature.

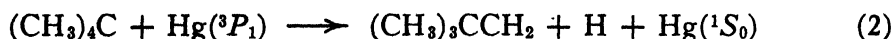
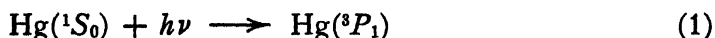
Discussion

Three points which are considered to merit discussion have been brought out in this investigation:—

- (a) The quantum yield in the initial stages is very low (0.004), and is independent of pressure, at 25°C .
- (b) The major products are hydrogen and dineopentyl.
- (c) The rates of production of hydrogen (and probably of dineopentyl) and methane are temperature dependent and indicate activation energies of about 4.3 and 5.1 kcal. per mole respectively.

(i) *The Nature of the Initial Act*

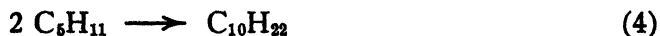
The great preponderance of hydrogen and dineopentyl in the products shows that the initial act may, with some confidence, be given as:—



It has been shown recently (8) that H atoms react readily with neopentane at room temperature, so that the reaction:—



will probably represent the fate of a considerable fraction of the H atoms produced in (2). Dineopentyl almost certainly arises from the recombination of the radicals produced in Reactions (2) and (3):—

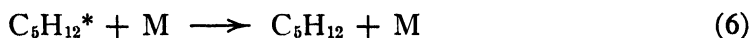


Thus neopentane behaves quite similarly to the other paraffin hydrocarbons with respect to the nature of the products. However, the above reactions, although they account adequately for the products, afford no explanation for the low quantum efficiency.

(ii) *Quantum Yield*

A recent estimate (1) of the effective cross section of neopentane in quenching $\lambda 2537$ shows that quenching is essentially complete under the conditions pertaining in the present investigation and that there is no indication that neopentane quenches to the metastable $\text{Hg}(^3P_0)$ state.

The inefficiency of the mercury photosensitized reactions of ethane in the medium pressure range has been accounted for (3) by recombination of H and C_2H_5 , and similar reactions:—



could certainly be responsible for some of the inefficiency in the present case. However, since the reactions of H with ethane and neopentane (3) are equally rapid at room temperature (8), it would be expected that the quantum yield of hydrogen production from ethane and neopentane would be similar, whereas it has been found to be lower by a factor of 100 with neopentane. Now Reaction (2) has been assumed to be the sole fate of the $\text{Hg}(^3P_1)$ atoms, and the above mechanism, by the usual stationary state treatment, gives

$$\phi_{\text{H}_2} = k_3 p / (k_3 p + k_5 [P]) \quad \text{or} \quad 1/\phi_{\text{H}_2} = 1 + k_5 [P] / k_3 p$$

where $[P]$ represents the pressure of the pentyl radical and p that of neopentane. For the low value of ϕ_{H_2} found $k_5 [P] / k_3 p$ must be large compared with unity, so that we may put

$$1/\phi_{\text{H}_2} = k_5 [P] / k_3 p \quad \text{and} \quad \phi_{\text{H}_2} = k_3 p / k_5 [P]$$

The presence of three possible recombinations, such as reactions (4) and (5) and the recombination of H atoms, leads to a rather complex equation for the dependence of $[P]$ on p . However, a graphical solution gives a curve which may be represented roughly by

$$[P] = ap^\alpha,$$

where a is a constant including k_3 and k_5 and α , though pressure dependent, lies in the interval $1/2 > \alpha > 0$. Hence we have

$$\phi_{\text{H}_2} = ap^{1-\alpha}.$$

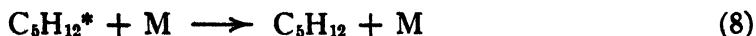
Now α varies from $1/2$ at very low pressures to a value approaching zero at high pressures which would lead to ϕ_{H_2} varying as a power of p between 1 and $1/2$. Such a pressure dependence would certainly have been found in the present investigation had it existed. Hence it is unlikely that the above recombination reactions could have been the major causes of the inefficiency. The 20-fold increase in rate on the addition of small amounts of hydrogen gives more definite evidence that the recombination reactions were not the major causes but that the inefficiency must be due to the actual quenching act, and leads to the belief that, although neopentane quenches effectively,

the energy obtained from the mercury atom is dissipated in some way without causing reaction to occur.

If it be assumed that the primary act is not as given by Reaction (2) but by



where $\text{C}_5\text{H}_{12}^*$ represents a neopentane molecule with excess energy, and that $\text{C}_5\text{H}_{12}^*$ may either decompose or be deactivated:—



we get

$$1/\phi_{\text{H}_2} = 1 + \frac{k_8}{k_7} p,$$

which requires a linear relation between $1/\phi_{\text{H}_2}$ and p , which is contrary to experiment.

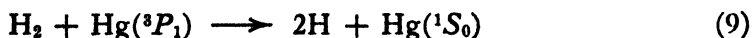
Hence it seems likely that the initial act proceeds by both Reactions (2) and (2') and that essentially all of the active neopentane molecules formed in (2') are deactivated by collision, i.e., the excited molecule has a long life. This gives

$$\phi_{\text{H}_2} = \frac{k_2}{k_2 + k'_2}$$

in the absence of added hydrogen and

$$\phi_{\text{H}_2} = \frac{k_2 p + 2k_9[\text{H}_2]}{(k_2 + k'_2)p + k_9[\text{H}_2]}$$

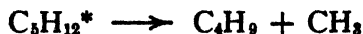
in the presence of hydrogen, where Reaction (9) is



Both the above relations agree, at least qualitatively, with the results obtained in the absence and presence of hydrogen.

(iii) *The Temperature Coefficient and the Production of Methane*

The fact that, at 25° C., the rate of production of methane increases with decreasing pressure makes it likely that methane arises, as in the similar reactions of ethane (3) and propane (2), by "atomic cracking", consisting of Reaction (5) and the decomposition of the active neopentane molecule formed:



Since the inefficiency of the reaction has been ascribed to the occurrence of Reaction (2') it is likely that the activation energy found (4.3 kcal.) for the production of hydrogen may be ascribed to an increase in the fraction $k_2/k_2 + k'_2$ with increasing temperature. Hence we may put $E_2 = 4.3$ kcal. It is significant that Morikawa, Benedict, and Taylor (5) found an almost identical value for the effect of temperature on the rate of production of

hydrogen in the mercury photosensitized reaction of methane. The activation energy found for the production of methane (5.1 kcal.) shows that the increase in the rate of formation of methane with increasing temperature cannot have been due to decomposition of the neopentyl radical, since the reaction



certainly has a very much higher activation energy. It is likely that the difference between the E 's for H_2 and CH_4 is not real and that the increase in the rate of methane formation runs parallel with that of hydrogen and, actually, is the natural consequence of the increased rates of production of H and C_5H_{11} with increasing temperature.

The results of this investigation show that, in the reaction with $\text{Hg}(^3P_1)$ atoms, neopentane resembles methane, the only other of the lower paraffins that is totally symmetrical, rather than ethane which has C-H bonds very similar to those in neopentane. Hence there is a strong probability that the symmetry of the hydrocarbon molecule plays an important part in its mercury photosensitized reactions. This is probably due to the long life of the active molecules formed in the quenching act.

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SYNTHETIC AND SPECTROMETRIC STUDIES OF SOME PYRAZOLONES¹

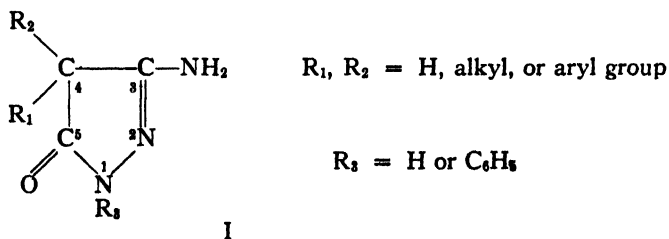
BY PAUL E. GAGNON, JEAN L. BOIVIN², AND R. NORMAN JONES

Abstract

Fourteen pyrazolones were synthesized from the corresponding mono or disubstituted cyanoacethydrazides or cyanoacetphenylhydrazides and evidence concerning their constitution was obtained from chemical reactions and ultra-violet absorption spectra determinations. A mixture of two tautomeric forms was obtained when 4-benzyl-3-amino-5-pyrazolone was prepared; it was converted to a single form by treatment with hydrochloric acid. The following compounds, as far as the authors are aware, have been prepared for the first time: 4-methyl-3-amino-5-pyrazolone, 4-methyl-2-phenyl-3-amino-5-pyrazolone, 4-ethyl-3-amino-5-pyrazolone, 4-ethyl-2-phenyl-3-amino-5-pyrazolone, 4-(2-phenoxyethyl)-3-amino-5-pyrazolone, 4-(2-phenoxyethyl)-2-phenyl-3-amino-5-pyrazolone, 4-(3-phenoxypropyl)-3-amino-5-pyrazolone, 4-(3-phenoxypropyl)-2-phenyl-3-amino-5-pyrazolone, 4-phenyl-3-amino-5-pyrazolone, 4-benzyl-3-amino-5-pyrazolone, 4-benzyl-2-phenyl-3-amino-5-pyrazolone, 4,4-dibenzyl-3-amino-5-pyrazolone, 4,4-dibenzyl-2-phenyl-3-imino-5-pyrazolone, 4,4-(2,2-spiro-indanyl)-3-amino-5-pyrazolone.

Introduction

The first investigations of 3-amino-5-pyrazolones (I) were carried out in 1906 by Conrad and Zart (2), who treated ethyl cyanoacetate with phenylhydrazine and obtained a product which they assumed to be 1-phenyl-3-hydroxy-5-pyrazolone. The compound proved to be of some importance in color photography (7). In 1941, Weissberger and Porter (9) prepared 1-phenyl-3-amino-5-pyrazolone from ethyl oxalacetate and phenylhydrazine and showed that the compound of Conrad and Zart was the same. In 1937, other 3-amino-5-pyrazolones were prepared by Hepner and Fajersztejn (4).



In 1947, Gagnon, Savard, Gaudry, and Richardson (3) observed that crude alkyl-cyanoacethydrazides, on standing for some time, underwent transformation to the corresponding 4-alkyl-3-amino-5-pyrazolones. These authors prepared for the first time 3-amino-5-pyrazolones substituted only in position 4.

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Contribution from the Department of Chemistry, Laval University, Quebec, and the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1903. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

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Pyrazolones substituted in positions 1 and 2 had already been reported (10, 11, 12, 13).

In the present work, the ultraviolet absorption spectrum of 1-phenyl-3-amino-5-pyrazolone, prepared from ethyl oxalacetate and phenylhydrazine, was determined (Fig. 1). Four different types of 4-substituted-5-pyrazolones were synthesized and their ultraviolet absorption spectra also measured.

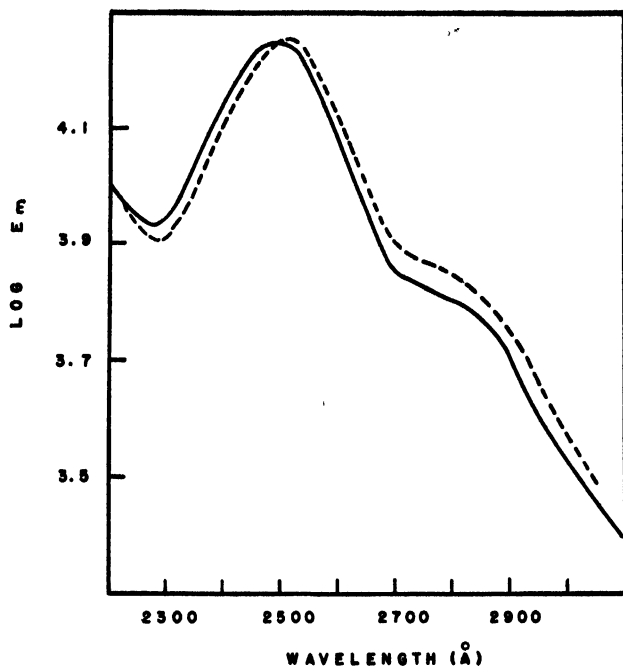


FIG. 1. Ultraviolet absorption spectra.

— 1-Phenyl-3-amino-5-pyrazolone (ethanol).

- - - 4-Methyl-2-phenyl-3-amino-5-pyrazolone (ethanol).

A. 4-Monosubstituted-3-amino-5-pyrazolones.—Six different compounds were prepared by treatment of the corresponding hydrazides with strong alkalis or by heating the substituted cyanoacetic esters with hydrazine hydrate in the presence of sodium ethylate. Cyclization occurred only in alkaline solution, although 4-methyl-3-amino-5-pyrazolone seemed to form in the absence of an excess of hydrazine. All these pyrazolones gave a color test with ferric chloride, indicating the presence of a potential phenolic group (8). The 4-benzyl derivative was obtained as a mixture of tautomers, and was transformed to one of them completely by acid catalysis.

B. 4-Monosubstituted-2-phenyl-3-amino-5-pyrazolones.—These pyrazolones were prepared by a modification of the method of Conrad and Zart (2). The ferric chloride test was negative; the compounds were soluble in strong alkalis.

C. 4,4-Disubstituted-3-amino-5-pyrazolones.—The pyrazolones were prepared by the method described for the 4-monosubstituted-3-amino-5-pyrazolones. A concentration higher than one equivalent of alkali per mole of pyrazolone precipitated the alkali salt.

D. 4,4-Disubstituted-2-phenyl-3-imino-5-pyrazolones.—These pyrazolones were also synthesized by a modification of the method of Conrad and Zart (2). These were insoluble in strong acids and were soluble in strong alkalis. The alkali salts were precipitated by adding an excess of sodium hydroxide.

Experimental†

The properties of the pyrazolones are summarized in Tables I and II. The yields ranged from 75 to 95%. The melting points are uncorrected.

TABLE I
GENERAL PROPERTIES OF PYRAZOLONES

Compound	Solubility*					Reactions	
	Water	Acids	Alkalies	NaHCO ₃	Ether	FeCl ₃	HNO ₃
4-Monosubstituted-3-amino-5-pyrazolones	s	s	s	i	i	Pos.	Pos.
4-Monosubstituted-2-phenyl-3-amino-5-pyrazolones	i	s	s	i	s	Neg.	Pos.
4,4-Disubstituted-3-amino-5-pyrazolones	s.s.	s	s.s.**	i	i	Pos.	Pos.
4,4-Disubstituted-2-phenyl-3-imino-5-pyrazolones	i	i	s.s.**	i	s	Neg.	Neg.

s = soluble, i = insoluble, s.s. = slightly soluble.

* Pyrazolones having an actual or potential hydroxyl group at 5 are soluble in water, insoluble in ether, and give a positive ferric chloride test. Pyrazolones lacking such a hydroxyl group are insoluble in water, soluble in ether, and give no color with ferric chloride (see page 21).

** A concentration of alkali higher than one equivalent per mole of pyrazolone precipitated the metal salt.

4-Monosubstituted-3-amino-5-pyrazolones

These compounds were prepared by the following methods:

(a) Crude monosubstituted cyanoacethydrazides (0.1 mole) were treated with sodium hydroxide (40%, 0.2 mole). The reaction was exothermic. The solutions were allowed to stand at room temperature for two hours and were neutralized with acetic acid (50%). The precipitates were filtered off, washed with ether to remove any substituted malonic acids formed in the reaction, and recrystallized several times from water or ethanol.

(b) To a solution of sodium ethoxide (0.2 mole of sodium and 80 ml. of absolute ethanol) was added a mixture of ethyl substituted cyanoacetates (0.1 mole) and hydrazine hydrate (100%, 0.1 mole). The solution was refluxed for half an hour on the water bath. The solvent was removed under reduced pressure, the residue dissolved in water (100 ml.), and the solution extracted with ether (50 ml.) to remove unchanged esters. The aqueous layer was neutralized with acetic acid and allowed to stand in a cold place, where a solid crystallized out.

† The methods of preparation of the compounds used to synthesize the different pyrazolones are given in a previous paper (Gagnon, P. E. and Boivin, J. L. *Can. J. Research*, B, 26 : 503, 1948.).

TABLE II
PROPERTIES OF INDIVIDUAL PYRAZOLONES

Compound	Formula	M.p., °C.	Analysis, %		Ultraviolet absorption maxima			
			Nitrogen		Neutral		Acid	
			Calc.	Found	Å	log E_m	Å	log E_m
4-Monosubstituted-3-amino-5-pyrazolones								
4-Methyl	C ₆ H ₇ ON ₃	242–243	41.6	41.7	2700	3.61	2600	3.68
4-Ethyl	C ₈ H ₉ ON ₃	247–248	33.1	32.5	2840	3.56	2700	3.50
4-(2-Phenoxyethyl)-	C ₁₁ H ₁₃ O ₂ N ₃	186–187	19.1	18.7	2780 2710 2430	3.26 3.34 4.05	2760 2700 2380	3.09 3.21 4.07
4(3-Phenoxypropyl)-	C ₁₃ H ₁₅ O ₂ N ₃	110–111	18.0	17.9	2780 2700 2460	3.42 3.46 4.06	2780 2700 2360	3.07 3.17 4.05
4-Phenyl	C ₉ H ₇ ON ₃	246–247	24.0	23.8	2560	4.21	2460	4.19
4-Benzyl	C ₁₀ H ₁₁ ON ₃	203–204	22.2	22.0	2470	4.08	2360	4.05
4-Monosubstituted-2-phenyl-3-amino-5-pyrazolones								
4-Methyl	C ₁₀ H ₁₁ ON ₃	227–228	22.2	22.1	2500	4.22	2660	4.23
4-Ethyl	C ₁₁ H ₁₃ ON ₃	213–214	20.7	20.8	2500	4.23	2680	4.11
4-(2-Phenoxyethyl)-	C ₁₇ H ₁₉ O ₂ N ₃	136–137	14.2	14.2	2560	4.26	2700	4.25
4-(3-Phenoxypropyl)-	C ₁₈ H ₁₉ O ₂ N ₃	108–109	13.6	13.4	2530	4.22	2700	4.16
4-Benzyl	C ₁₈ H ₁₉ ON ₃	160–161	15.9	15.3	2520	4.15	2700	4.21
4,4-Disubstituted-3-amino-5-pyrazolones								
4,4-Dibenzyl	C ₁₇ H ₁₇ ON ₃	242–243	14.0	15.0	2760	3.57	2660	3.60
4,4-(2,2-spiro-Indanyl)-	C ₁₁ H ₁₁ ON ₃	238–239	20.9	20.8	2740 2670	3.73 3.70	2730 2660	3.74 3.76
4,4-Disubstituted-2-phenyl-3-imino-5-pyrazolones								
4,4-Dibenzyl	C ₂₃ H ₂₃ ON ₃	259–260	11.8	12.1	2760	3.55	2760	3.59

4-Methyl-3-amino-5-pyrazolone.—Ethyl- α -cyanopropionate (12.7 gm., 0.1 mole) was stirred with hydrazine hydrate (100%, 5.0 gm., 0.1 mole). The mixture was placed in an evacuated desiccator or left standing at room temperature. After two weeks, crystals appeared and after a month, the whole material was solid. It was recrystallized from ethanol. The ferric chloride test was positive.

4-Ethyl-3-amino-5-pyrazolone.—Ethyl- α -cyanobutyrate (14.1 gm., 0.1 mole) was stirred with hydrazine hydrate (100%, 5.0 gm., 0.1 mole). The solution

was allowed to stand at room temperature, whereupon solidification took place. The white solid was treated with two equivalents of sodium hydroxide. The reaction was exothermic. The resulting solution was allowed to stand at room temperature for two hours, when crystals appeared. The mixture was neutralized with dilute acetic acid and evaporated to dryness on the water bath. The material was extracted with ethyl acetate in a Soxhlet during 12 hr. The solvent was removed under reduced pressure and the residue recrystallized several times from ethanol. The ferric chloride test was positive.

4-Benzyl-3-amino-5-pyrazolone.—This compound was prepared by Method (b). A sharp melting point could not be obtained in spite of many recrystallizations from water; m.p. 200° to 204° C. Since the ultraviolet absorption spectra determinations on this pyrazolone indicated that it was probably a mixture of two molecular species, it was thought that acids as catalysts might produce only one tautomer, and alkalis reverse the reaction. The following results indicate that hydrochloric acid catalyzed the transformation of one tautomer into another, which was not affected by further treatment with sodium hydroxide. The material (5 gm.), melting between 200° and 204° C., was then refluxed for half an hour in a normal solution of hydrochloric acid in water. The reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in a normal solution of sodium hydroxide in water and the resulting solution was neutralized with dilute acetic acid. A solid separated out on standing in a cold place. It was filtered out, washed with ether, and recrystallized from a fairly large volume of water: m.p. 203° to 204° C. Yield, quantitative. The ferric chloride test was positive.

4-Monosubstituted-2-phenyl-3-amino-5-pyrazolones.—To a solution of sodium ethoxide (0.2 mole of sodium and 80 ml. of absolute ethyl alcohol) was added a mixture of ethyl substituted cyanoacetates (0.1 mole) and phenylhydrazine (10.8 gm., 0.1 mole). The mixture was heated at 160° C. in an oil bath for 18 hr. The solvent was removed under reduced pressure, the residue dissolved in water (100 ml.) and extracted with ether to remove unchanged esters. An oily product separated out on acidification with acetic acid and soon solidified. It was washed with dilute sodium carbonate to remove any substituted malonic acids formed in the reaction, and recrystallized from ethanol.

4,4-Disubstituted-3-amino-5-pyrazolones.—To a solution of sodium ethoxide (0.2 mole of sodium and 80 ml. of absolute ethyl alcohol) was added a mixture of the ethyl disubstituted cyanoacetate (0.1 mole) and hydrazine hydrate (100%, 0.1 mole). The reaction mixture was refluxed for two hours in an oil bath maintained at 160° C. The solvent was removed under reduced pressure. The residue was dissolved in hot water (100 ml.). On cooling, the sodium salt of the pyrazolone crystallized out. It was separated by filtration, washed with ether and finally with dilute hydrochloric acid. The filtrate was extracted with ether to remove unchanged ester. The aqueous layer was neutralized with acetic acid and allowed to stand in a cold place. The crystals formed were combined with the solid material previously obtained. The solid

mixture was washed with ether, to remove any disubstituted malonic acids formed in the reaction, and recrystallized several times from a large volume of water.

4,4-Disubstituted-2-phenyl-3-imino-5-pyrazolones.—These pyrazolones were prepared by the method outlined above for the 4,4-disubstituted-3-amino-5-pyrazolones, but phenylhydrazine was used instead of hydrazine and the time of heating in an oil bath was 18 hr.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra were determined on a Beckman spectrophotometer; the experimental details have been reported previously (3). The data are plotted in Figs. 2–9. The spectra may be divided into two distinct groups, designated the “high intensity” and the “low intensity” type, in Table III.

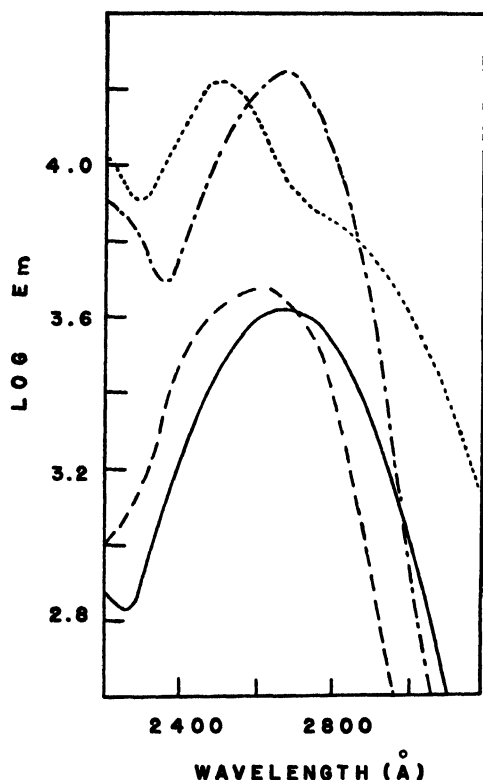


FIG. 2.

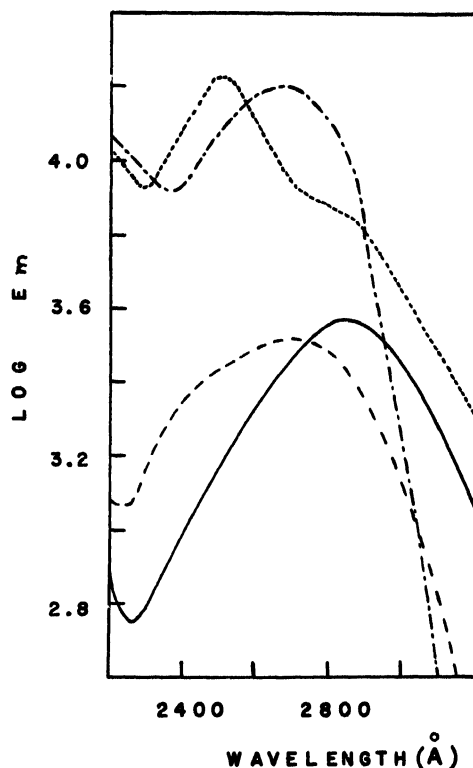


FIG. 3.

FIG. 2. Ultraviolet absorption spectra.

- 4-Methyl-3-amino-5-pyrazolone (ethanol)
- - - (N hydrochloric acid in 90% ethanol).
- 4-Methyl-2-phenyl-3-amino-5-pyrazolone (ethanol)
- · - · - (N hydrochloric acid in 90% ethanol).

FIG. 3. Ultraviolet absorption spectra.

- 4-Ethyl-3-amino-5-pyrazolone (ethanol).
- - - (N hydrochloric acid in 90% ethanol).
- 4-Ethyl-2-phenyl-3-amino-5-pyrazolone (ethanol).
- · - · - (N hydrochloric acid in 90% ethanol).

TABLE III
CLASSIFICATION OF ULTRAVIOLET ABSORPTION SPECTRA

Compound	Acid shift on principal maximum	Proposed structure
<i>A. High intensity type spectra</i>		
4-Benzyl	Hypsochromic (-110 Å)	XX
4-(2-Phenoxyethyl)-	" (-50)	XX
4-(3-Phenoxypropyl)-	" (-100)	XX
4-Phenyl	" (-100)	XX
4-Methyl-2-phenyl-	Bathochromic (+160)	XXI
4-Ethyl-2-phenyl	" (+180)	XXI
4-Benzyl-2-phenyl-	" (+180)	XXI
4-(2-Phenoxyethyl)-2-phenyl	" (+140)	XXI
4-(3-Phenoxypropyl)-2-phenyl	" (+170)	XXI
<i>B. Low intensity type spectra</i>		
4-Methyl-	Hypsochromic (-100)	XXIII (or XXII)
4-Ethyl-	" (-140)	XXIII (or XXII)
4,4-Dibenzyl-	" (-100)	XXIII (or XXII)
4,4-(2,2-spiro-Indanyl)-	" (-10)	XXIII (or XXII)
4,4-Dibenzyl-2-phenyl-	— (Nil)	XXII

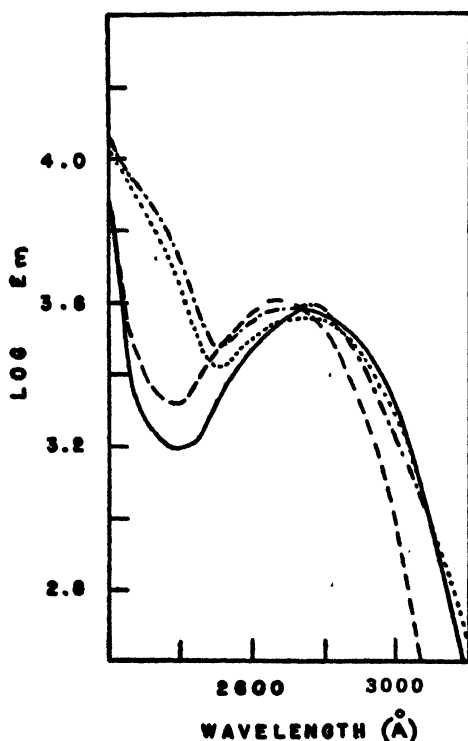


FIG. 4.

FIG. 4. Ultraviolet absorption spectra.

— 4,4-Dibenzyl-3-amino-5-pyrazolone (ethanol).

--- " " (N hydrochloric acid in 90% ethanol).

..... 4,4-Dibenzyl-2-phenyl-3-imino-5-pyrazolone (ethanol).

- - - - - " " (N hydrochloric acid in 90% ethanol).

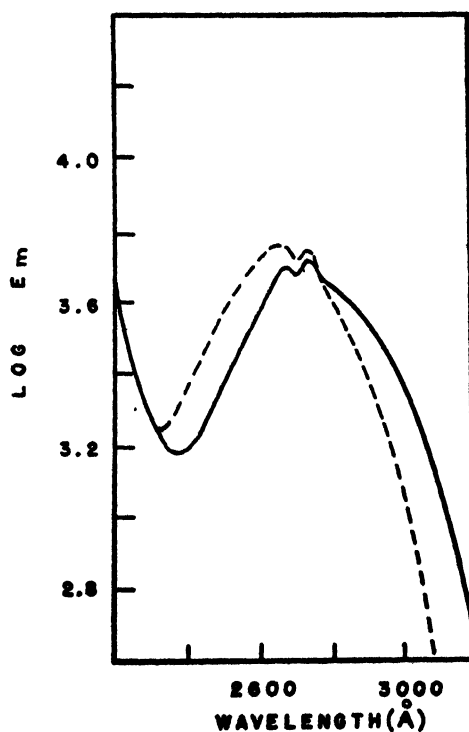


FIG. 5.

FIG. 5. Ultraviolet absorption spectra.

— 4,4-(2,2-spiro-Indanyl)-3-amino-5-pyrazolone (ethanol).

--- " " (N hydrochloric acid in 90% ethanol).

The spectra of the 4-monosubstituted-3-amino-5-pyrazolones are not all similar. The simple 4-methyl and 4-ethyl derivatives (Figs. 2, 3) possess a broad band of relatively low intensity with a maximum at 2700 to 2900 Å. The position of the maximum is shifted hypsochromically in acid medium. The spectrum of 4,4-dibenzyl-3-amino-5-pyrazolone is similar (Fig. 4).

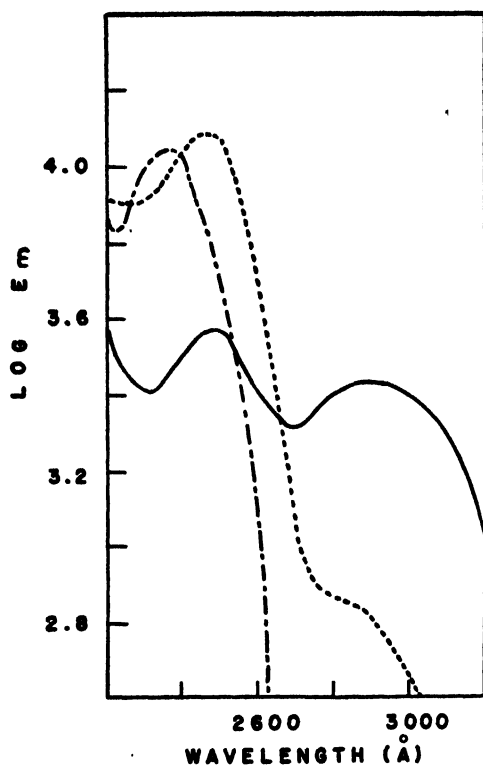


FIG. 6.

FIG. 6. *Ultraviolet absorption spectra.*

- 4-Benzyl-3-amino-5-pyrazolone (ethanol), before refluxing with acid.
 --- Ditto. (after refluxing with acid).
 - · - · - Ditto. (in *N* hydrochloric acid in 90% ethanol).

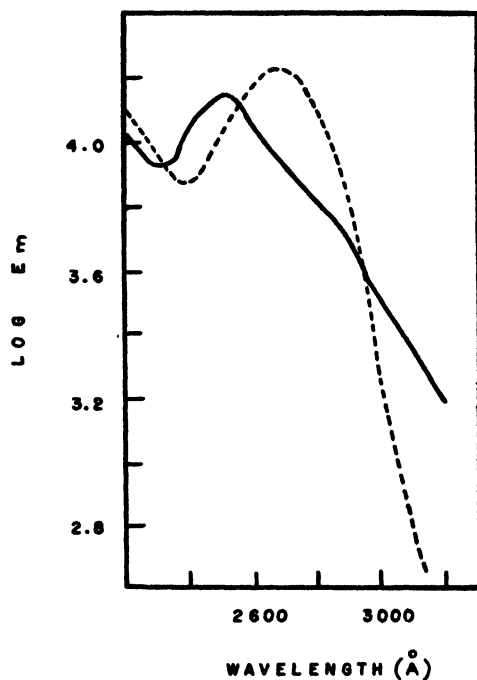


FIG. 7.

FIG. 7. *Ultraviolet absorption spectra.*

- 4-Benzyl-2-phenyl-3-amino-5-pyrazolone (ethanol).
 --- " " " " " (*N* hydrochloric acid in 90% ethanol).

The curve of the 4-monobenzyl derivative differs considerably from those of the 4-methyl and 4-ethyl compounds. As initially prepared it exhibited two separate maxima (Fig. 6). This, in conjunction with the broad range of the melting point (200°–204° C.), suggested a mixture of products, possibly tautomers; after refluxing with acid the product obtained melted sharply (203°–204° C.) and gave a spectrum with a single peak. This maximum is more intense than that of the 4-methyl and 4-ethyl compounds and lies at considerably shorter wave-lengths. This indicates a difference in the ring chromophore, since the phenyl group in the side chain cannot be in conjugation with the ring, and its additive contribution to the total absorption of the molecule would be negligible (5).

In the spectra of the 4-(2-phenoxyethyl)- and 4-(3-phenoxypropyl)- derivatives (Figs. 8 and 9) the additive contribution of the side chain chromophores to the total absorption is quite large. In Fig. 10 the curve obtained by sub-

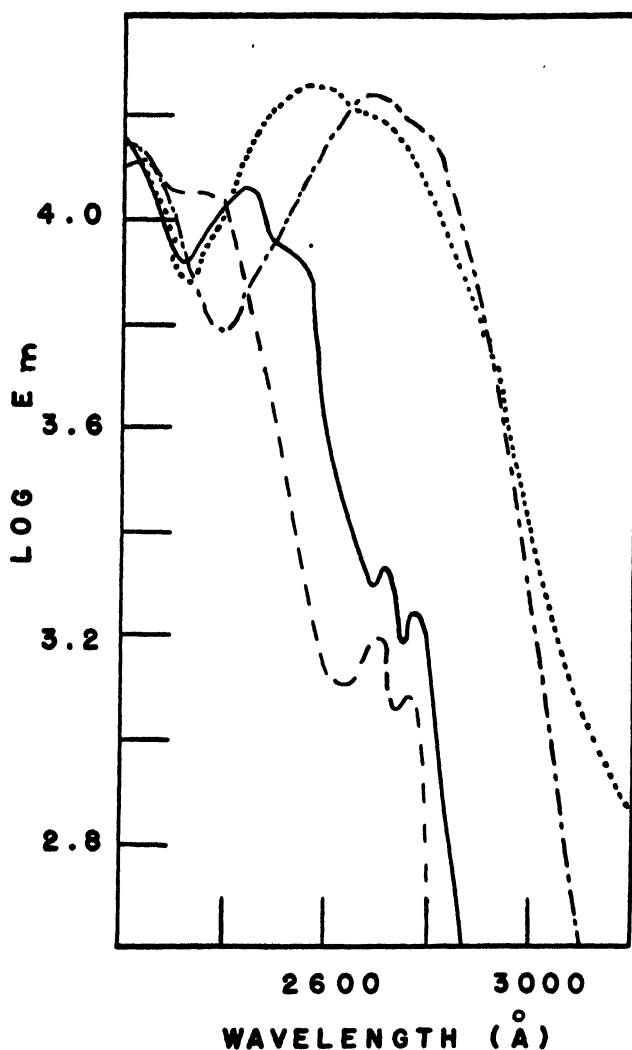


FIG. 8. Ultraviolet absorption spectra.

- 4-(2-Phenoxyethyl)-3-amino-5-pyrazolone (ethanol).
- - - " " " " (N hydrochloric acid in 90% ethanol).
- 4-(2-Phenoxyethyl)-2-phenyl-3-amino-5-pyrazolone (ethanol).
- · - · - " " " " (N hydrochloric acid in 90% ethanol).

traction of the spectrum of phenetol from that of 4-(2-phenoxyethyl)-3-amino-5-pyrazolone is compared with the spectrum of the 4-benzyl compound. The evident similarity shows that in the 4-phenoxyalkyl derivatives the ring structure is similar to that of the 4-benzyl compound and different from that of the 4-methyl compound.

The spectrum of 4-phenyl-3-amino-5-pyrazolone (Fig. 11) is also similar in general type to that of the 4-benzyl compound but it is shifted by some

100 Å to longer wave lengths. This would be in accord with a basic ring system similar to that of the 4-benzyl derivative; the bathochromic shift resulting from the extra conjugation of a phenyl group attached directly to

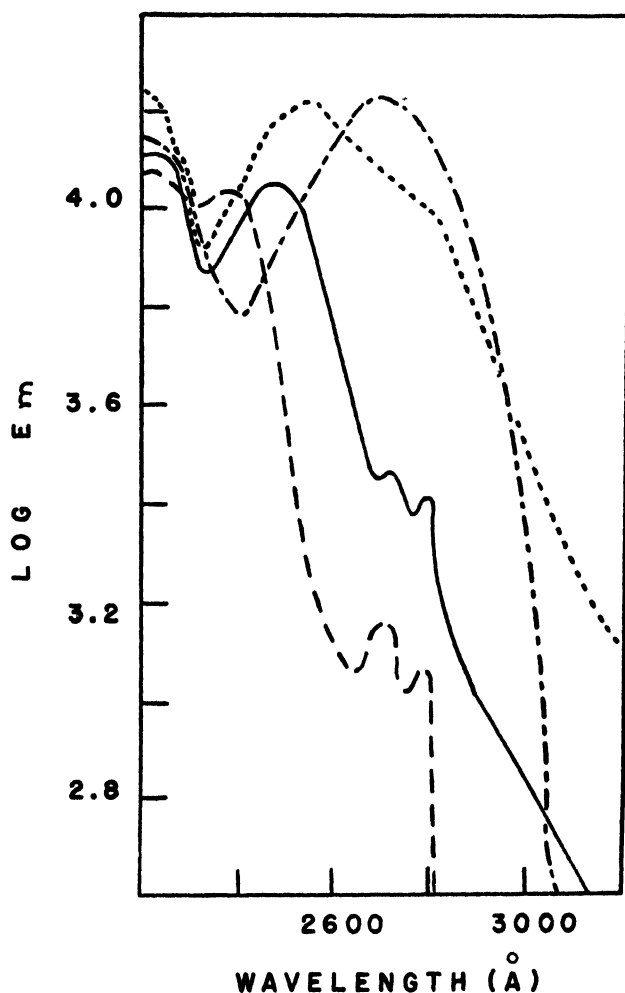


FIG. 9. Ultraviolet absorption spectra.

- 4-(3-Phenoxypropyl)-3-amino-5-pyrazolone (ethanol).
 --- " " " (N hydrochloric acid in 90% ethanol).
 4-(3-Phenoxypropyl)-2-phenyl-3-amino-5-pyrazolone (ethanol).
 -.-.- " " " (N hydrochloric acid in 90% ethanol).

the heterocyclic ring. It is to be noted that in all these 4-monosubstituted compounds, the spectra are shifted to shorter wave-lengths in acid.

The spectra of the 4-monosubstituted-2-phenyl-3-amino-5-pyrazolones differ from those of the corresponding derivatives which lack the 2-phenyl group (Figs. 2-4, 7-9). The absorption is more intense and on the addition of acid the curves are displaced, bathochromically or not significantly altered (Table III).

4,4-Dibenzyl-2-phenyl-3-imino-5-pyrazolone (Fig. 4) possesses a spectrum with a single maximum of lower intensity similar to that of the 4-methyl and 4,4-dibenzyl derivatives. On acidification the position of the maximum is not changed.

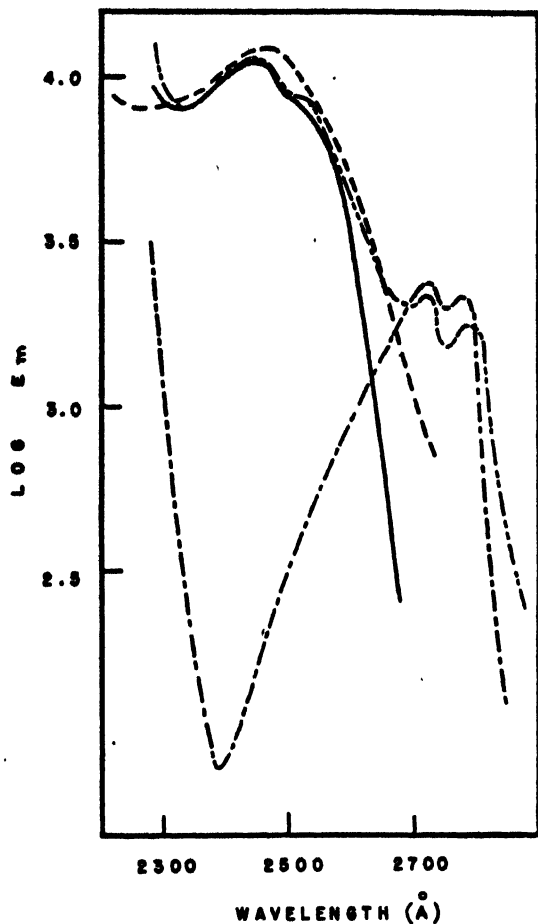


FIG. 10.

FIG. 10. Ultraviolet absorption spectra.

- A - - - - Phenetol (ethanol).
 B - ····· 4-(2-Phenoxyethyl)-3-amino-5-pyrazolone (ethanol).
 C - - - 4-Benzyl-3-amino-5-pyrazolone.
 D ——— Calculated curve obtained by subtraction of Curve A from Curve B.

FIG. 11. Ultraviolet absorption spectra.

- 4-Phenyl-3-amino-5-pyrazolone (ethanol).
 - - - " " " (N hydrochloric acid in 90% ethanol).

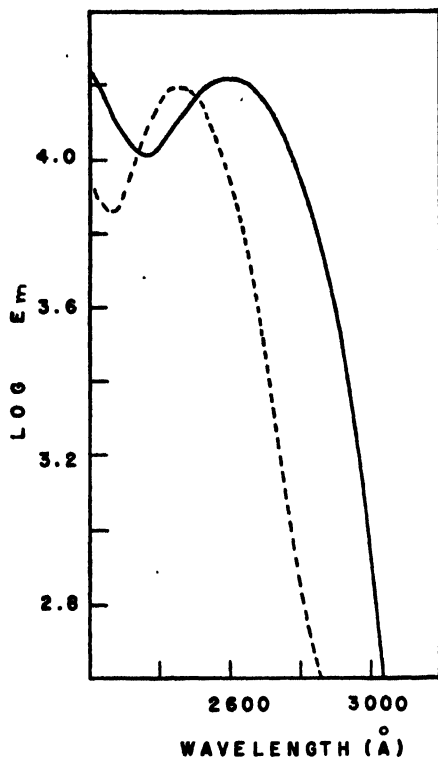


FIG. 11.

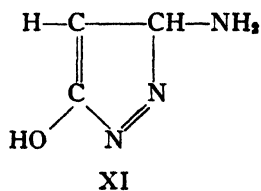
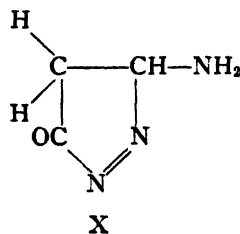
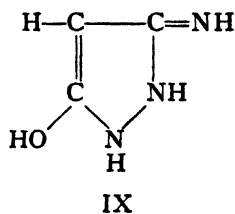
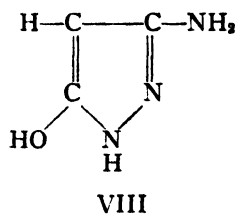
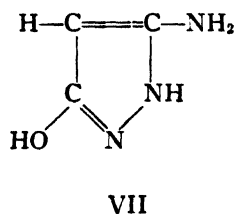
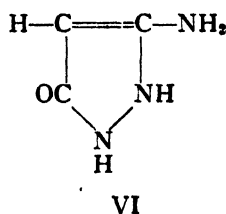
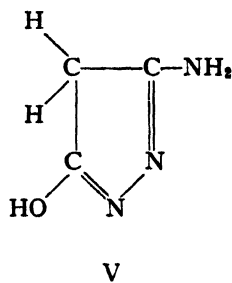
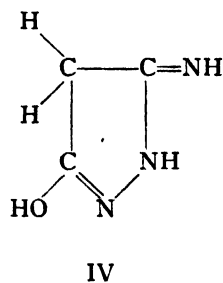
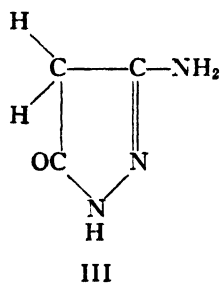
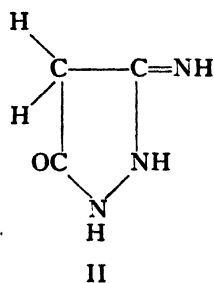
Discussion

Assuming, on the basis of the elemental analyses and general chemical behavior, that these compounds all contain the pyrazolone ring system, the differences observed in the absorption spectra must be associated with different tautomeric forms.

It is not possible, from the spectra, to distinguish unequivocally among the several possible tautomeric forms, but a comparison of the absorption curves does reveal that the spectra fall into well defined classes, as shown in Table III. This classification is based on the shape and intensity of the curves and on the direction of the displacement in acid.

In the following discussion, an attempt is made to relate the spectra with specific tautomeric forms. The arguments presented are frankly speculative and alternative interpretations are probably possible. The chemical evidence of structure derived from the ferric chloride and nitrous acid tests (Table I) is considered also in relation to the spectrographic data.

The 10 tautomeric structures II–XI represent the basic formulae which may be considered a priori for 3-amino-5-pyrazolone, and the 4-monosubstituted derivatives may be written in terms of any of these. In the 4,4-disubstituted derivatives the choice is restricted to II, III, IV, V, and X. The 4-monosubstituted-2-phenyl derivatives may have structures II, IV, VI, VII, or IX, but for the 4,4-disubstituted-2-phenyl-3-imino-5-pyrazolones only II and IV are possible.

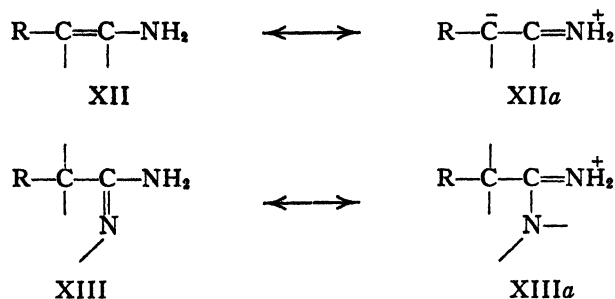


Displacement of Spectra on Acidification

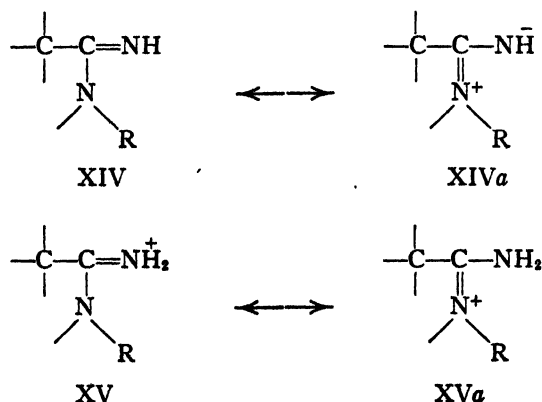
Consideration of the spectra indicates that, in addition to their classification in terms of intensity, the compounds may be divided into those in which the absorption maximum is displaced considerably to shorter wave lengths on

acidification (hypsochromic), and those in which the displacement is bathochromic or negligible.

Displacement to shorter wave lengths on acidification is very suggestive of an amino group directly attached to a conjugated system, as in the partial structures XII and XIII. In the neutral molecule these may resonate with XIIa and XIIIa, but on acidification the possibility of this type of resonance is lost in the amine ion. This behavior is seen commonly in the spectra of aromatic amines (6) and would be expected from pyrazolones having the structures III, V, VI, VII, VIII, X, and XI.



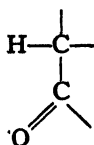
The type of structure which might give rise to a shift to longer wave lengths on acidification is not so easily recognized. One possibility might be the imino structure XIV. In the ionic form XV resonance can occur with XVa, the system bearing a formal analogy with that of a carbocyanine dye, the spectrographic properties of which have been examined extensively by Brooker (1). In the neutral molecule, resonance between the analogous structures XIV and XIVa would be suppressed by the separation of charge and the instability of the $-\text{NH}^-$ group. On the basis of this argument one might expect a shift to longer wave lengths on acidification of pyrazolones having structures II, IV, IX.



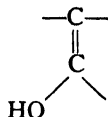
Significance of Ferric Chloride and Nitrous Acid Reactions

The development of color on addition of ferric chloride in acid solution is generally regarded as indicative of a phenolic hydroxyl group (8), either present in the molecule as such or readily derived as a result of an equilibrium

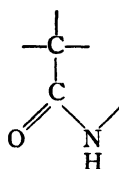
displacement. In the 3-amino-5-pyrazolones the partial structures XVI–XIX are indicated by a positive response to this test. The liberation of nitrogen on addition of nitrous acids identifies a structure possessing an actual or potential free primary amino group.



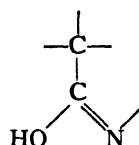
XVI



XVII



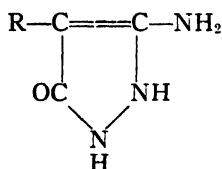
XVIII



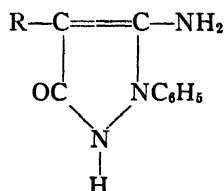
XIX

Structure of Compounds with High Intensity Spectra

These compounds (Table III) include both 4-monosubstituted and 4-monosubstituted-2-phenyl-3-amino-5-pyrazolones. If it is assumed that the similarity of the spectra is indicative of a similar chromophoric system in the two groups of compounds, modified only by the extra conjugation from the phenyl group, structures of Types II, IV, VI, VII, and IX are alone open for consideration. In the ferric chloride reaction the 4-monosubstituted compounds give a positive and the 4-monosubstituted-2-phenyl derivatives a negative reaction, and, of the structures listed above, only type VI will satisfy this criterion. On this evidence structures XX and XXI may be proposed for the compounds giving the high intensity spectra.



XX



XXI

This conclusion is consistent with the positive reaction in the nitrous acid test, and the solubility behavior (Table I). It accounts also for the hypsochromic displacement of the spectra of the 4-substituted-3-amino-5-pyrazolones on acidification.*

It does not account however for the bathochromic displacement of the spectra of the 2-phenyl derivatives in acid, at least in terms of the mechanism proposed in Formulae XIV and XV which require an imino group at position 3.

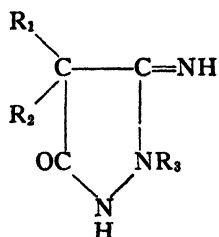
Compounds Giving Low Intensity Spectra

This group (Table III) includes 4-monosubstituted, 4,4-disubstituted, and 4,4-disubstituted-2-phenyl-3-imino-5-pyrazolones. If the similarity of the

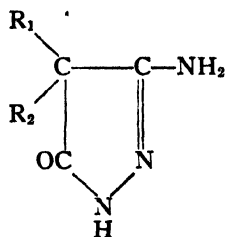
* The spectrum of 4-phenyl-3-amino-5-pyrazolone conforms closely to that of the 4-benzyl derivative but the maximum is displaced by 100 Å to longer wave lengths. This shift suggests that the phenyl group is conjugated with the ring chromophore, and is also consistent with structure XX for these compounds.

spectra is indicative of a common chromophoric system, only structures of types II and IV are open for consideration. Both of these would be expected to give a positive ferric chloride color test for the 4-mono- and 4,4-disubstituted derivatives, and a negative response for the 4,4-disubstituted-2-phenyl derivatives. These conclusions are in agreement with the experimental facts (Table I). On the basis of this evidence structures XXII and XXIII are equally plausible. The positive reaction with nitrous acid given by the 4-mono, and the 4,4-disubstituted compounds would suggest XXIII as the preferred structure, and this is in agreement also with the hypsochromic shift of the spectrum on acidification. On the other hand, structure XXII is to be preferred for the 4,4-disubstituted-2-phenyl compounds on account both of the nonreaction with nitrous acid and the small bathochromic shift of the spectrum in acid.

In conclusion, it must be emphasized that these assignments of structure based on evidence from ferric chloride and nitrous acid tests, and from similarity (but not identity) of spectra, can only be considered as tentative. The mechanism proposed for the bathochromic displacement of the spectra of certain of the compounds in acid solution is not always consistent with the evidence for the presence of a free amino group, as indicated by a positive reaction with nitrous acid. It may also be significant that the compounds which exhibit a strong bathochromic shift of the absorption maximum on acidification all contain the 2-phenyl substituent.



XXII



XXIII

R_1 = Alkyl R_2 = H or alkyl R_3 = H or C_6H_5

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THE MOLECULAR ADSORPTION AREAS OF HYDROCARBON GASES ON CHARCOAL¹

BY M. A. NAY² AND J. L. MORRISON

Abstract

The low temperature adsorptions of methane, ethane, propane, normal butane, isobutane, acetylene, ethylene, and nitrogen on a series of coconut charcoals of different degrees of activation were determined. Langmuir isotherms were obtained in every case. The measurements indicate horizontal orientation of the hydrocarbon molecules on the charcoal surface. By comparing the maximum number of millimoles adsorbed for each gas on each charcoal with the respective maximum number of millimoles of nitrogen adsorbed, and by assuming a molecular adsorption area of 16.2 \AA^2 for nitrogen, the following average molecular adsorption areas were obtained: methane—19.4, ethane—25.9, propane—36.0, normal butane—42.1, isobutane—47.4, acetylene—19.8, and ethylene—23.1 \AA^2 .

Introduction

In the determination of the surface areas of adsorbents by gases, it is important to know the area occupied by the molecules of the adsorbed gas. The development of the B.E.T. equation (4) and the concomitant method for determining the amount of adsorption in a single molecular layer have given a new impetus to estimations of such molecular adsorption areas.

In this paper, measurements of the adsorption of most of the simple aliphatic hydrocarbon gases on a charcoal series of different degrees of activation are reported. It was considered that such measurements would reveal the orientation of the hydrocarbon molecules on a charcoal surface. Similar measurements with aliphatic acids adsorbed from aqueous solutions (14) indicated vertical orientation of the acids at the charcoal-water interface.

McIntosh and his collaborators (11) have measured the adsorption of nitrogen and normal butane on a similar charcoal series. They *assume* that the butane is horizontally oriented on the charcoal surface and they calculate charcoal areas on this basis. Others (1, 5, 8, 9, 13) have measured the adsorption of a few hydrocarbon gases and nitrogen on various surfaces, including some carbon blacks. By comparing the hydrocarbon with the nitrogen adsorption, and by assuming a definite value for the area occupied by the nitrogen molecule, they have obtained results suggesting horizontal adsorption of the hydrocarbons on the various adsorbents.

Experimental

Materials

Nitrogen was obtained from tank nitrogen, by passing the tank nitrogen successively through chromous chloride solution (to remove oxygen), driers, and a liquid air trap.

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Pure methane was obtained by the low temperature fractionation (liquid air) of Viking natural gas (91% methane, 3.3% other hydrocarbons, 5.7% nitrogen) using a column described by Freeth and Verschoyle (12).

Pure ethane was prepared by the hydrolysis of ethylmagnesium bromide. The gas was passed through scrubbers and fractionated in the same way as the methane.

Helium (98.2%) from the Ohio Chemical Company was used. Prior to storage in a bulb, the helium was purified by being passed through an activated charcoal trap cooled in liquid air.

Ethylene (99.5%), propane (99.9%), normal butane (99.9%), and isobutane (99%), obtained from the Ohio Chemical Company, were purified further by fractionating each once at 40° to 50° C. below their respective boiling points.

Commercial acetylene was purified in the same manner as the methane and ethane. Prior to fractionation, the gas was passed through scrubbers to remove soluble impurities (10, p. 167).

The charcoals were samples of a series of coconut charcoals of different degrees of activation produced by the Standard Chemical Company of Montreal. The series is the same as that used by Lemieux and Morrison (14), in whose paper some data on their properties are given.

Method

The adsorption isotherms of the gases were determined by means of an apparatus similar to the one described by Emmett (6, p. 3). The principal volumes, other than the adsorption bulb, were water-jacketed to control the gas temperature. These temperatures were measured to 0.5° accuracy. Pressures were measured to the nearest 0.05 cm. of mercury.

Samples of 0.20 to 0.25 gm. charcoal were placed in an adsorption bulb of about 2.5 ml. volume. The dead space was determined at 0° C. with helium. When the adsorptions of the various gases were measured, temperatures several degrees above the boiling points of the respective gases had to be used. Although the theory of the B.E.T. equation suggests the boiling points of the adsorbing gases as the adsorption temperatures, the higher temperatures were necessary because it was found that charcoal exhibited the phenomenon of capillary condensation at the lower temperatures. The boiling points of the gases and the adsorption temperatures are given in Table I.

The nitrogen bath contained liquid air. Acetylene, ethylene, and ethane temperatures were obtained by immersing a liquid air finger in an acetone bath; propane and isobutane temperatures were obtained by dry ice - acetone baths, and normal butane by an ice-water bath.

A special constant temperature bath had to be devised for methane. A pyrex test tube wound with 5 ft. of 20 gauge nichrome resistance wire was fitted into a larger test tube. The assembly was immersed in liquid air,

with the inner test tube as the cooling chamber for the charcoal bulb. A copper-constantan thermocouple was fixed to the adsorption bulb and a regulated electric current through the nichrome wire controlled the temperature to within $\pm 1^\circ \text{C}$.

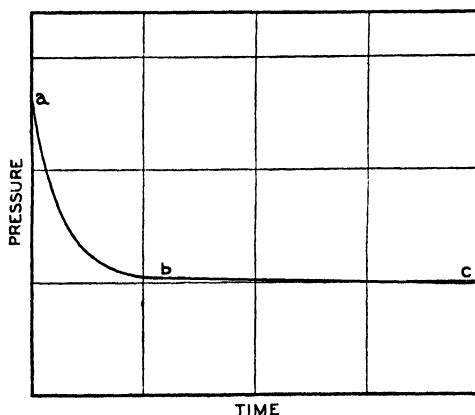
TABLE I

BOILING POINTS AND ADSORPTION TEMPERATURES OF GASEOUS ADSORBATES

Gas	Boiling point, $^\circ\text{K}$.	Temp. of adsorption bath, $^\circ\text{K}$.
Nitrogen	77.4	83
Methane	111.7	128
Acetylene	191.4	198
Ethylene	169.3	183
Ethane	184.9	195
Propane	231.0	234
<i>n</i> -Butane	272.8	273
Isobutane	263.0	265

Some attempt was made to avoid an arbitrary choice of the time of equilibrium. This arbitrariness arises from the porous nature of coconut charcoal. At first, an arbitrary time of 10 min. for the initial adsorption step and about five minutes for each subsequent adsorption step was used. However, much more consistent data were obtained when the estimated equilibrium times were based on experimental measurements made in some preliminary time studies of the adsorption process.

The rates of adsorption of several of the gases on Charcoals 1 and 6 were measured, by following the pressure drop with time after admission of the gas

FIG. 1. *Typical pressure-time curve for the adsorption process.*

to the adsorption bulb. A plot of the pressure against time always gave curves typically represented by Fig. 1.

It is considered that the first part *ab* of the curve mainly represents pure adsorption and the second part *bc* represents adsorption after diffusion into

very fine pores. The time for adsorption equilibrium is taken as at *b*. The results of these measurements are given in Table II for those gases that are starred. The steps in the adsorption process are the successive admissions of gas at increasing pressures. The initial step is always the largest in this type of work.

TABLE II

TIME ALLOTTED (MINUTES) FOR ADSORPTION EQUILIBRIUM TO BE ATTAINED

Steps in adsorption process	Charcoal No. 1							
	CH ₄ *	C ₂ H ₆ *	C ₃ H ₈ *	<i>n</i> -C ₄ H ₁₀	<i>iso</i> -C ₄ H ₁₀ *	C ₂ H ₄	C ₂ H ₂ *	N ₂ *
1	30	20	15	10	10	25	30	25
2	10	10	10	7	7	15	15	20
3	5	5	5	4	4	5	10	15
4	5	5	5	4	4	5	5	10
5	5	5	5	4	4	5	5	5
6	5	5	5	4	4	5	5	5
	Charcoal No. 6							
	CH ₄	C ₂ H ₆ *	C ₃ H ₈	<i>n</i> -C ₄ H ₁₀ *	<i>iso</i> -C ₄ H ₁₀	C ₂ H ₄	C ₂ H ₂ *	N ₂ *
1	15	15	25	30	30	20	20	15
2	10	10	15	20	20	10	10	10
3	5	5	10	10	10	5	5	5
4	5	5	5	10	10	5	5	5
5	5	5	5	5	5	5	5	5
6	5	5	5	5	5	5	5	5

The times allotted to the other gases and charcoals were estimated by interpolation.

Results

All the gases used in these experiments gave practically straight lines when the data were plotted according to the linear form of Langmuir's equation;

$$p/v_a = \frac{1}{v_m b} + p/v_m$$

in which v_a is the volume of gas (reduced to S.T.P.) adsorbed at the pressure, p . In Figs. 2 and 3, the plots of the equation are shown for nitrogen and normal butane. These and similar plots were used to calculate v_m , which represents the volume adsorbed in a single molecular layer, and, in the case of charcoal, the maximum adsorption (2, p. 292; 3). The experimental results are given in this form in Table III.

The volumes in Table III were not corrected for deviations from ideality. Calculations on normal butane, which exhibits the largest deviations, did not give a measurable difference from the ideal case, probably because the adsorptions are relatively large and the dead space is relatively small (about 2.4 ml. at S.T.P.) (7).

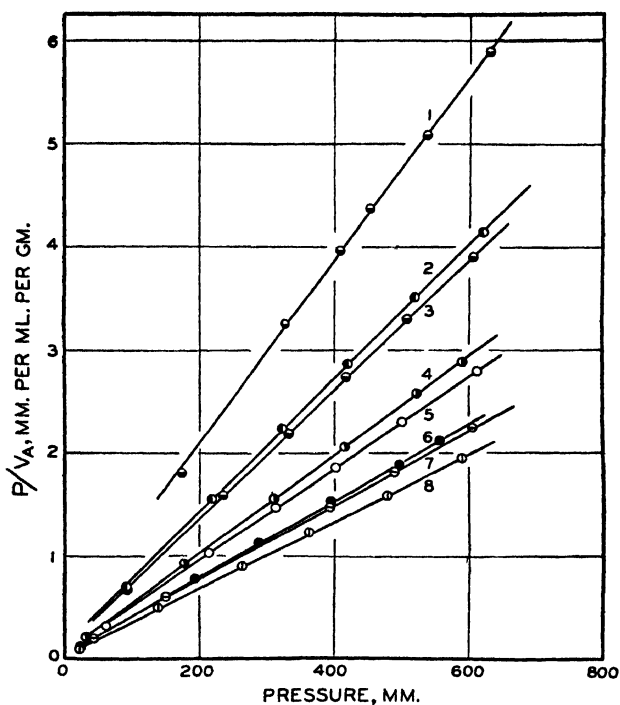
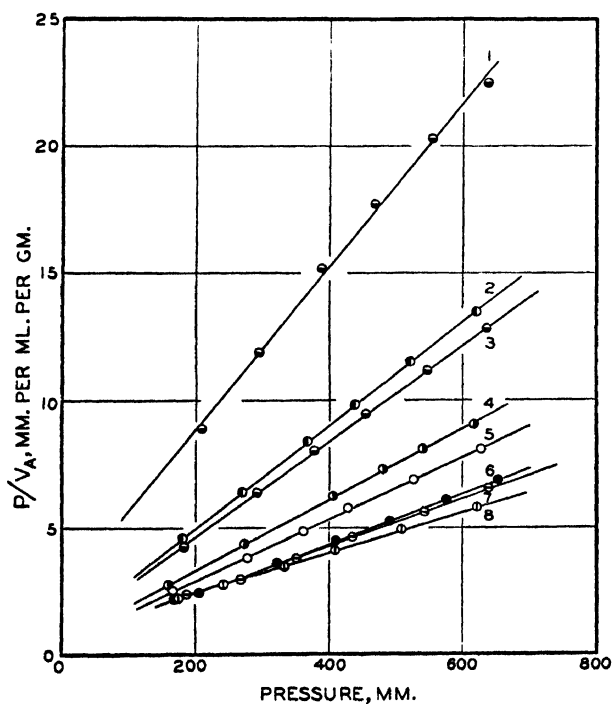
FIG. 2. *Langmuir plots for adsorption of nitrogen on charcoal series.*FIG. 3. *Langmuir plots for adsorption of normal butane on charcoal series.*

TABLE III

MAXIMUM ADSORPTION OF GASES IN MILLIMOLES PER GRAM OF CHARCOAL

Adsorbate	Charcoal number							
	1	2	3	4	5	6	7	8
N ₂	5.08	6.72	7.08	9.30	9.98	11.83	12.35	13.77
C ₂ H ₂	5.50	6.01	6.10	7.72	8.39	9.57	10.09	11.04
C ₂ H ₄	4.03	5.06	5.18	6.70	7.02	8.20	8.63	9.46
CH ₄	4.28	5.82	6.12	7.75	8.38	9.76	10.18	10.96
C ₃ H ₆	3.28	4.25	4.44	5.87	6.18	7.35	7.79	8.37
C ₃ H ₈	1.77	2.73	2.88	3.96	4.39	5.47	5.59	6.13
<i>n</i> -C ₄ H ₁₀	1.36	2.20	2.39	3.23	3.70	4.55	4.77	5.49
<i>iso</i> -C ₄ H ₁₀	1.18	1.59	1.78	2.70	3.46	4.02	4.24	4.66

Discussion

The nitrogen v_m values are different from the values given in the paper of Lemieux and Morrison (14) for the *same* charcoal series. The differences arise from sampling. Larger samples cannot be used in this type of work, so that the differences are unavoidable. However, they are not significant to the present paper.

Adsorption and Diffusion

The preliminary time studies indicate that two processes are occurring, which for convenience will be called primary and secondary adsorptions. Although not completely separable, these processes are apparently of sufficiently different rates to be partially separated. The primary adsorption is by far the more rapid process. The experiments were carried out at such a pace as to make the secondary adsorption effect negligible, an objective believed to have been achieved in the case of the more active Charcoals 5 to 8. For these charcoals, the points of the Langmuir plots were in each case on one straight line. On the other hand, for the less active charcoals, and particularly for the larger adsorbate molecules (cf. *n*-butane in Fig. 3) there is a tendency for the points to lie on a curve concave to the pressure axis. The curvature may be explained by the secondary adsorption process which would tend to be cumulative—increasing v_a at a more rapid rate than would have been given by the primary adsorption process alone.

The less active charcoals are also characterized by having a larger proportion of smaller pores (11, 14). Thus the secondary adsorption process probably involves diffusion into very small pores.

Orientation and Area of Adsorbed Molecules

In Fig. 4, the maximum adsorptions of the straight chain hydrocarbon gases are compared in the same way as Lemieux and Morrison (14) had compared the maximum adsorptions of the aliphatic acids. The v_m for each gas is plotted against the v_m of normal butane, for each charcoal.

In the case of the adsorption of the aliphatic acids from solution on the same charcoal series, similar plots gave parallel lines at low activation of the charcoal, and converging lines at high activation. In contrast, the hydrocarbon gases give diverging lines with increasing charcoal activity.

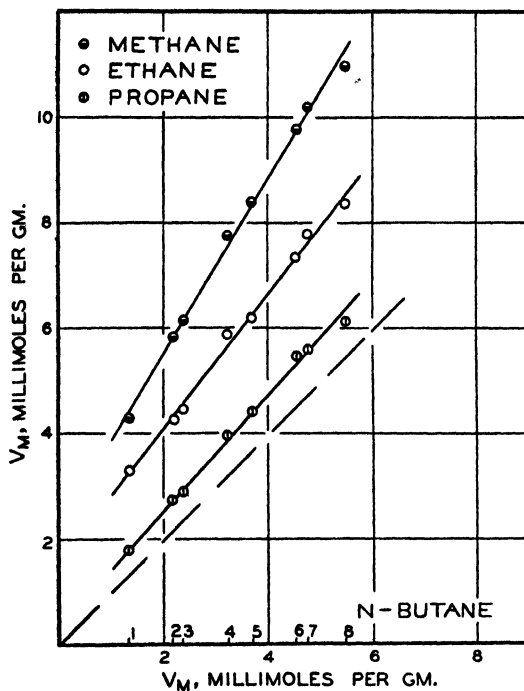


FIG. 4. Comparison of v_m , the maximum adsorptions, of methane, ethane, and propane with that of normal butane.

In general, increasing the activation of charcoal increases the amount of adsorption of every adsorbate, whether aliphatic acid or hydrocarbon gas. Also, for any asymmetric adsorbate, the extreme alternatives for the packing of the molecules on the surface are vertical and horizontal orientations. By plotting v_m of each adsorbate against the v_m of a particular one (the comparisons must be made among molecules with about the same cross-sectional area), it is possible to obtain some indication of which of these orientations is occurring. If the orientation is vertical, the lines will be either coincident or parallel, coincident if all adsorbate molecules reach the same internal area and displaced but parallel if they do not. The results of the adsorption of the straight chain aliphatic acids from water solutions were interpreted to indicate vertical orientation of the acid molecules in the saturated adsorbed layer (14). On the other hand, when the orientation is horizontal, the v_m plots will consist of a series of divergent lines, the divergence increasing with charcoal activation. It is considered that the results as plotted in Fig. 4 suggest horizontal orientation of the hydrocarbon gas molecules on the charcoal surface.

Calculations of the effective adsorption areas of the hydrocarbon molecules also strongly suggest horizontal orientation. Assuming that nitrogen occupies an area of 16.2 \AA^2 per molecule (5, p. 1246), the effective adsorption areas of the other gases are calculated to be equal to

$$\frac{v_m(\text{N}_2)}{v_m(\text{gas})} \times 16.2,$$

and are given in Table IV. The average molecular adsorption areas are based on the underlined values. The exclusion of the other values is suggested by the following discussion.

TABLE IV
MOLECULAR ADSORPTION AREAS OF GAS MOLECULES IN SQUARE ANGSTROMS

Adsorbate	Charcoal number								Average
	1	2	3	4	5	6	7	8	
C_2H_2	15.0	18.1	18.8	19.5	19.3	20.0	19.8	20.2	19.8 ± 0.3
C_3H_4	20.4	21.5	22.1	22.5	23.0	23.4	23.2	23.6	23.1 ± 0.3
CH_4	19.2	18.7	18.7	19.4	19.3	19.6	19.7	20.4	19.4 ± 0.4
C_2H_6	25.1	25.6	25.8	25.7	26.2	26.1	25.7	26.7	25.9 ± 0.4
C_3H_8	46.5	39.9	39.8	38.1	36.8	35.1	35.8	36.4	36.0 ± 0.6
$n\text{-C}_4\text{H}_{10}$	60.5	49.5	48.0	46.6	43.7	42.1	42.0	40.7	42.1 ± 0.8
$iso\text{-C}_4\text{H}_{10}$	69.7	68.5	64.4	55.8	46.8	47.7	47.2	47.9	47.4 ± 0.4

The magnitude of the average molecular adsorption areas as well as the v_m plots indicate horizontal adsorption. Moreover, it is generally indicated that activated coconut charcoal has a variety of pore sizes; thus, accessibility to the internal surface of a particular charcoal will depend on the size of the adsorbate molecule. If the hydrocarbons do adsorb horizontally on charcoal, then their accessibility to the internal surface of a particular charcoal will depend on their molecular thicknesses. The thinner molecules will reach more internal surface than the thicker ones. The effective molecular adsorption areas shown in Table IV indicate that molecular thickness is the determining factor in the accessibility of the hydrocarbon gases to the charcoal surface.

The adsorption areas are relative to that of nitrogen. Therefore, the accessibility as shown by these areas also will be relative to the thickness of the nitrogen molecule. Molecules thinner than the nitrogen molecule will reach larger internal surfaces than nitrogen; as a result the molecular adsorption areas for these molecules will be too low compared with their true values. The converse will be true for molecules thicker than nitrogen. The results in Table IV fall into three groups, (1) molecules with adsorption areas that

increase with charcoal activation (acetylene and ethylene), (2) those that remain the same (methane and ethane) and (3) those that decrease (propane and the two butanes). In every case, steady values are reached at higher charcoal activations. Probably the explanation for the development of the steady values is that all the gases including nitrogen reach about the same internal surface for each of Charcoals 5 to 8.

The results in Table IV suggest that for the hydrocarbon molecules considered here there are three groups of thicknesses, (1) acetylene and ethylene, (2) methane and ethane and (3) propane and the two butanes. It would appear that, compared with the nitrogen molecule, the first group is thinner, the second about the same, and the third thicker. If the average molecular adsorption areas in Table IV are incorrect, it may be argued that the correct molecular adsorption areas would be less for molecules thicker than nitrogen and greater for molecules thinner than nitrogen.

The molecular adsorption areas will probably be related to van der Waals areas. Pauling (15, p. 189) gives the van der Waals radii for some of the gases discussed here. The van der Waals radii refer to solid or liquid packing and not to the *thickness* of molecules in isolation (i.e., in a monomolecular layer). Nevertheless, some indication of thickness should be given by the van der Waals diameters. Thus, nitrogen should be approximately 3 Å thick, and methane and ethane about 4 Å thick. Pauling assigns the ethylene group the same van der Waals radius as the methyl group, which is valid for end to end contact of the molecules. However, the atomic structure of ethylene, with its nonrotation about the double bond, suggests a smaller thickness than for ethane and a thickness similar to acetylene. The results in Table IV support this suggestion.

Further, if propane were to lie as flat as possible on the charcoal surface, it would have the same molecular thickness as methane and ethane. Experimentally, however, propane has about the same thickness as the two butanes. Apparently, the adsorption forces holding propane to the charcoal surface are not sufficient to restrict free rotation about its single carbon-carbon bonds.

Comparisons may be made with existing measurements of molecular adsorption areas (all referred to nitrogen = 16.2 Å²). Data are available for acetylene (8), normal butane (1, 5, 8, 9, 13) and 1-butene (1, 5) on various adsorbents. For normal butane adsorbed on various carbon blacks, Beebe and his collaborators (1) found values of 39.7, 41.4, 43.7 and 45.1 Å². On the same adsorbents they found areas for 1-butene ranging from 37.8 to 40.6 Å². Emmett and Cines (8) obtained areas of 49 Å² for normal butane and 22.2 Å² for acetylene, both on porous glass. Further, they found (9) areas of 52 and 41 Å² for normal butane on two samples of zinc dust, and an area of 42 Å² on a carbon black. From their work with several adsorbents, Harkins and Jura (13) assign a value of 54 Å² for normal butane. Similarly, from results for various metal foils and powders, Davis, DeWitt, and Emmett (5) assign a value of 46.9 Å² for normal butane and 42.7 Å² for 1-butene.

It is a simple matter to calculate the areas of the various charcoals by combining the values of the maximum adsorption of the various gases given in Table III with the respective average values in Table IV. The areas of Charcoals 1 to 4 will differ according to the gas used. But it would appear from the results given in Table IV that all gases reach the same internal areas for each of Charcoals 5, 6, 7, and 8.

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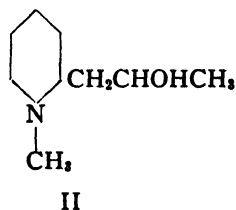
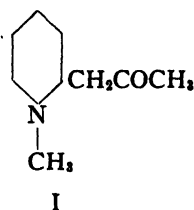
A NEW OCCURRENCE OF dl-METHYLISOPELLETIERINE¹

BY LÉO MARION AND MARCEL CHAPUT

Abstract

An investigation of *Sedum sarmentosum* Bunge has shown that this plant contains two liquid alkaloids which give rise to crystalline picrates. One of these bases proved to be *dl*-methylisopelletierine, identical with a synthetic specimen.

The previous isolation of alkaloids from a species of *Sedum* (2) prompted the examination of another plant belonging to the same genus. This latter plant, *Sedum sarmentosum* Bunge, has been introduced from China and cultivated in gardens. A quantity of this plant, grown in a local garden and kindly identified by Dr. H. A. Senn of the Botany Division, Dominion Experimental Farm, Ottawa, has now been examined. It has been found to contain two alkaloids, *A* and *B*, both of which were colorless liquids. The picrate of *A* gave identical analytical figures and had the same melting point as the picrate of *dl*-methylisopelletierine, one of the alkaloids of the bark of the pomegranate tree (*Punica granatum* L.) (4). The picrate of *B* contained two hydrogen atoms more than that of *A*. Meisenheimer and Mahler (3), who first synthesized *dl*-methylisopelletierine, or 1-(α -N-methylpiperidyl)-propan-2-one (I), obtained it by the mild oxidation of 1-(α -N-methylpiperidyl)-propan-2-ol (II)



and the recorded melting point of the picrate of the latter was very close to that of the picrate of *B*. It thus appeared probable that the two alkaloids isolated from *S. sarmentosum* might be represented by formulae I and II. Methylisopelletierine (I) was, therefore, synthesized by the method of Wibaut and Kloppenburg (5); the synthetic *dl*-base had the same boiling point as the first alkaloid (*A*) isolated from the plant and formed a picrate which did not depress the melting point of the picrate of the latter on admixture.

Reduction of the synthetic base with lithium aluminum hydride gave rise to the compound II. However, the picrate of this product when mixed with the picrate of base *B* caused a slight depression in melting point. Since II contains two asymmetric carbon atoms, the synthetic product must be a mixture of two pairs of enantiomorphs that will have to be separated and resolved before the identity of base *B* can be established.

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Experimental

The dried and ground plant material, weighing 1420 gm., was extracted with methanol in Soxhlets. The combined extract was acidified with hydrochloric acid to congo red and heated on the steam bath until the methanol had been largely evaporated. The residue was diluted with water, heated on the steam bath for several hours, allowed to cool, and kept in the refrigerator for several days. The mixture was filtered and the insoluble cake washed with a little water and again heated with dilute hydrochloric acid. This mixture was again cooled, filtered, and the two filtrates combined, alkalized with ammonia and extracted with 12 portions of chloroform. The solvent was distilled from the combined extract and the residue dissolved in dilute hydrochloric acid. This solution was filtered, extracted repeatedly with ether (discarded), alkalized with ammonia, and again extracted exhaustively with ether. This second extract, after drying over potassium hydroxide pellets, was distilled on the steam bath to remove the solvent. There was left an oily basic residue, wt. 2.0 gm., yield, 0.14% of the weight of the dried plant. The crude base was distilled *in vacuo* when the bulk boiled below 80° C. (0.4 mm.) and when redistilled, was obtained as a colorless oil, b.p. 72° to 75° C. (0.4 mm.), wt. 1.0 gm.

Isolation of Methyloisopelletierine (Alkaloid A)

The colorless oil described above was dissolved in methanol and added to a solution of picric acid in methanol. After concentration on the steam bath and subsequent standing at room temperature, the resulting solution deposited a picrate as clusters of needles which, after several recrystallizations from methanol-ether and one from absolute ethanol, was obtained as lemon yellow needles, m.p. 159° C.* Found: C, 47.11, 47.30; H, 5.47, 5.27; N, 14.38%. Calc. for $C_{15}H_{20}O_8N_4$: C, 46.88, H, 5.21; N, 14.58%.

The base was recovered from the picrate and redistilled *in vacuo*. A quantity of the base (61 mgm.) was then dissolved in absolute ethanol and the solution made up to exactly 2 cc. In a micropolarimeter tube this solution was found to exhibit no optical rotation.

Isolation of Alkaloid B

The methanolic mother liquor from which the picrate of alkaloid A had separated was evaporated down to a thick oil which was dissolved in boiling water. On cooling, this solution deposited a second picrate which, after two more recrystallizations from boiling water, consisted of fine, long, lemon yellow needles, m.p. 125° C. Found: C, 46.62; 46.48; H, 5.94, 5.91; N, 14.34, 14.37%. Calc. for $C_{15}H_{22}O_8N_4$: C, 46.63; H, 5.70; N, 14.51%.

The base recovered from the picrate was redistilled and used for the determination of the optical rotation: $[\alpha]_D^{25} 25.0$, $c = 2.48$ in absolute ethanol.

* All melting points are corrected

Synthesis of dl-Methylisopelletierine (I)

Crude 1-(α -pyridyl)-propan-2-one, prepared as described by Beets (1), was purified by conversion to the picrate in methanol solution. The filtered picrate, recrystallized twice from boiling methanol and twice from boiling benzene, melted at 141° C. The base recovered from the purified picrate was converted to the crystalline metho-sulphate and reduced in glacial acetic acid over Adams' catalyst (5); yield, 15 to 20%. The crude *dl*-methylisopelletierine was converted to the picrate which, after three recrystallizations from anhydrous ethanol, melted at 160° C. either alone or after admixture with the picrate of alkaloid A.

Dihydromethylisopelletierine

To a solution of lithium aluminum hydride (120 mgm.) in anhydrous ether (10 cc.), kept in a flask filled with a nitrogen atmosphere, was slowly added a solution of synthetic *dl*-methylisopelletierine (257 mgm.) in absolute ether (20 cc.). The resulting solution was refluxed for 30 min., cooled, and treated with water added dropwise until the excess reagent and addition compound were decomposed. The mixture was made strongly basic with sodium hydroxide and repeatedly extracted with ether. The combined extract was dried over potassium hydroxide pellets and the solvent distilled off. It left an oily residue which was dissolved in ether and added to an ethereal solution of picric acid. A mixture of oil and crystals was deposited on standing. The crystals when recrystallized from ether melted at 126° C. However, a mixture of this picrate with the picrate of alkaloid B melted at a slightly lower temperature.

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THE NITROLYSIS OF HEXAMETHYLENETETRAMINE

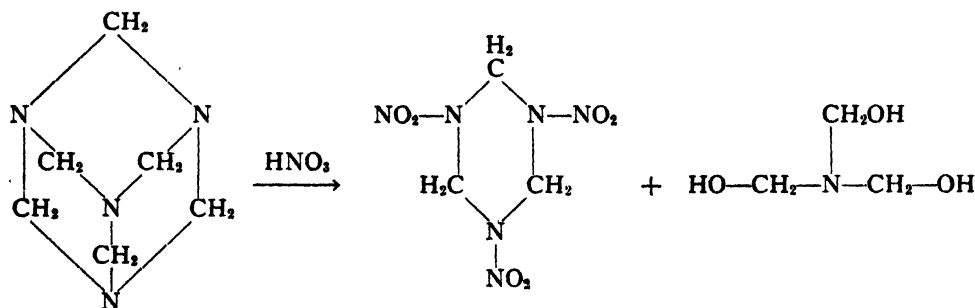
I. THE SIGNIFICANCE OF 1,5-ENDOMETHYLENE-3,7-DINITRO-1,3,5,7-TETRAZACYCLOOCTANE (DPT)¹

By W. J. CHUTE,² D. C. DOWNING,² A. F. MCKAY, G. S. MYERS,² AND
GEORGE F WRIGHT

Abstract

The nitrolysis of hexamethylenetetramine by the method of Hale yields, in addition to Cyclonite, an aqueous diluate which contains either dimethylol-nitramide, its dinitrate ester, or both. The presence of dimethylolnitramide can be demonstrated by its condensation with methylenediamine to give 1,5-dinitro-3,7-endomethylene-1,3,5,7-tetrazacyclooctane (DPT). The latter compound was identified by nitrolysis to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. The validity of the Mannich-type condensation of dimethylolnitramide from the Hale diluate (or from formaldehyde and nitramide) to form DPT has been attested by similar condensations with methylamine, ethylenediamine, cyclohexylamine, and benzylamine. In one of these condensations acetaldehyde has replaced part of the formaldehyde. Dimethylolnitramide has further been characterized by its conversion to 3,7-dinitro-3,7-diaza-1,5-dioxacyclooctane. Nitrolysis of the latter forms *sym.* dinitroxydimethylnitramide, which can be acetylated to *sym.* diacetoxydimethylnitramide.

The nitrolysis of hexamethylenetetramine (hexamine) described in detail by Hale (4) for the preparation of the explosive Cyclonite seems to involve the fission of at least three C-N linkages.



Hale found that 11 parts by weight of nitric acid were required for maximum yield, which decreased from 74.4% as the strength of nitric acid was decreased from 99.8%, until with 92% nitric acid he was able to recover 14.6% of his hexamethylenetetramine as the dinitrate salt.

Repetition of Hale's work indicated that the yield could be raised to a maximum of 86% crude (average 83%) by careful attention to the rate of addition of hexamine so as to avoid local decomposition. Optimum yields resulted from addition to 21 moles of 99.5 to 99.9% nitric at 20° to 25° C. over a 30 min. period. The reaction mixture was then drowned in ice.

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² Holders of Studentships under the National Research Council of Canada, 1941-1942.

When the Cyclonite had been filtered from this drowned liquor, neutralization of the filtrate to pH 5 in the cold with ammonia or other alkali precipitated a compound; it was decomposed by alkalies so that care was necessary in the neutralization, especially since precipitation was slow and was accompanied by the regeneration of acid. Maximum yield from any certain reaction mixture was obtained by cold neutralization with close attention to pH drift until pH 7 was finally reached. This behavior indicated that a reaction was occurring which was more complex than simple salt neutralization.

This substance will be proved to be 1,5-*endomethylene*-3,7-dinitro-1,3,5,7-tetrazacyclooctane and is conveniently called DPT (7), an abbreviation of the alternate name, dinitropentamethylenetetramine.

Yield correlation of this substance with Cyclonite formation and reaction conditions is summarized in a series of experiments recorded in Table I.

TABLE I
YIELD CORRELATION, DPT, AND CYCLONITE IN HALE PROCESS

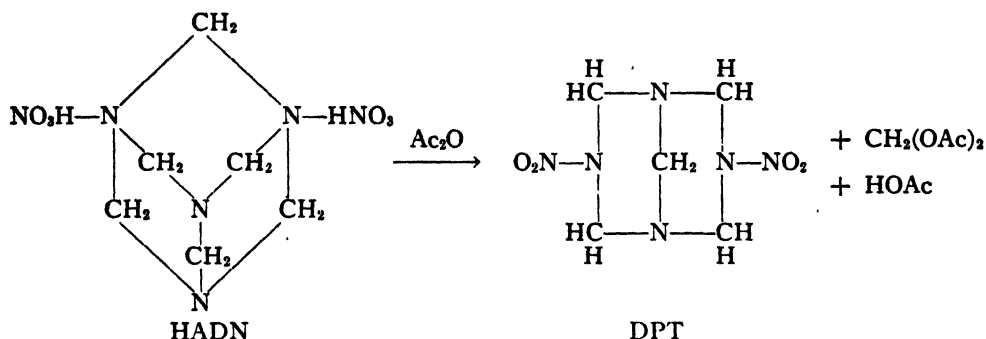
Experiment No.	1	2	3	4	5	6	7	8
Av. reaction time, min.	7	7	10	90	90	7	90	90
Av. reaction temp. °C.	-15	30	30	30	30	30	30	30
Moles hexamine	1	1	1	1	1	1	1	1
Conc. nitric acid, %	99	99	99	99	99	99	95	99
Moles nitric acid	20	20	20	20	10	10	20	40
% yield, Cyclonite	42	79	79	78	55	47	74	70
M.p. Cyclonite	198	201	194	198	201	196	198	200
% yield, DPT	5.6	18	16	9.3	18.3	23.4	12.3	<1
M.p. DPT	195	195	198	196	194	198	194	190

It is apparent from this table that DPT or its precursor is not very stable, since the yield is higher with shorter reaction time (Expts. 2,3,4 and also 5,6), especially when the nitric acid excess is high (Expt. 2 *versus* Expt. 6, and 7 *versus* 8). The yields of the two products seem to be related, as seen from Expts. 1 and 2, but not directly according to Expts. 2 and 7; probably through a common precursor.

The compound when purified for analysis showed an indefinite melting point with decomposition at 203° to 206° C. The sublimate arising from the thermal decomposition was a mixture of paraformaldehyde and hexamine, and 25 weight % of the latter compound could be obtained after long reflux of the DPT in ethanol. It decomposed in boiling water to yield 76% of its weight as formaldehyde. DPT was soluble in dilute acids and could be reprecipitated by neutralization, but at a pH of 3.4 rather than the pH of 5.2 when it was originally formed from the Hale reaction liquors. It therefore could function as a base, but its solution as a salt was unstable. Recoveries from cold nitric or hydrochloric acid varied from 58% to 12%, depending on the strength of acid and age of the solution. These data, together with the

elemental analysis conforming to $C_6H_{10}N_6O_4$, indicated that the substance was dinitropentamethylenetetramine, specifically 3,7-dinitro-1,5-*endome*-thylene-1,3,5,7-tetrazacyclooctane.

The compound could not be obtained by oxidation of the known dinitrosopentamethylenetetramine (3) but its structure was demonstrated by other methods. The composition of hexamine dinitrate (HADN) and DPT differ by one molecule of formaldehyde and one of water, and a dehydrating agent might convert one into the other. In conformity with the formulation, a slurry of hexamine dinitrate in 4 moles of acetic anhydride gave a 31% yield



of crude DPT after two days, about half of which was recovered by vacuum evaporation of the acetic acid and anhydride. The reaction was slow because of its heterogeneous nature, but a longer reaction time of four days decreased the yield to 17%.

The compound could also be produced from hexamine dinitrate in sulphuric or stabilized nitric acid media. DPT quickly decomposed in 90% sulphuric acid with gas evolution, but 82% could be recovered from an equal weight of 86% aqueous sulphuric acid, partly because it was not entirely soluble. It was not too surprising, then, that a hexamine dinitrate solution in cold 90% sulphuric acid gave, after neutralization with ammonia to pH 6.5, a 31% yield of DPT; the water formed in the reaction was sufficient to reduce the sulphuric acid concentration to a strength at which DPT was not decomposed appreciably. However, the high pH at which this precipitation occurred is more indicative of synthesis during addition of base (as in the original preparation) than of pre-formed DPT sulphate neutralization. The sulphuric acid synthesis, however useful, cannot therefore be considered to be a structure proof. Likewise the 5% yield obtainable from hexamine, nitric acid, and ammonium nitrate on neutralization with ammonia is probably formed during the neutralization and thus does not specify the structure of DPT.

Indeed this formation of DPT during neutralization of the Hale reaction liquors indicated that a precursor was present which was a degradation product of hexamine in strong acid solution. Knowledge of the behavior of this precursor during the neutralization phenomenon would contribute largely to structure proof of DPT. Conversely, separate proof of DPT structure would substantiate the nature of the precursor and would, perhaps, indicate

the mechanism of hexamine nitration. Since demonstration of this precursor is therefore critical to knowledge of this chemistry, it is unfortunate that it has never been isolated. The study of its behavior and mode of formation do, however, present, in the ensuing argument, a fairly reasonable assurance of its existence.

The nature of the precursor was first indicated by a reaction (7) in which nitramide in water was treated with six equivalents of formaldehyde and then neutralized with ammonia. At pH 5.6 to 6.5 a precipitate of DPT appeared over a five minute period, somewhat more rapidly, but in the same manner as from the diluted Hale nitration liquors. The yield was 73% on the nitramide basis, but gas evolution indicated that nitramide was decomposing. Repetition using four equivalents (excess) of nitramide per six equivalents of formaldehyde gave an 83% yield of DPT on the formaldehyde basis. The solution of formaldehyde and ammonia must be fresh, otherwise the yield is negligible. Since formaldehyde and ammonia condense irreversibly to form hexamine, it is not surprising that no yield of DPT can be obtained from nitramide, hexamine, and ammonia.

While these experiments themselves contributed little to structure proof of DPT, they established yield bases for evaluation of the next reaction, which utilized the methylenediamine sulphate, II, prepared by Knudsen (5) from methylenediformamide and sulphuric acid. When an aqueous solution of 2.7 moles of this salt was added to four moles of formaldehyde and four moles (excess) of nitramide and the resulting cold solution was then neutralized with sodium carbonate to pH 7, a yield of DPT precipitated immediately, which was 97% of theory on the formaldehyde basis, or 73% on the total methylene basis (if Knudsen's compound had decomposed entirely to formaldehyde). The high yield and rapid reaction thus justify the formulation shown on page 223.

Since nitramide is notoriously unstable in acid (or basic) solution, there is no possibility that it could be the DPT precursor from the Hale dilution liquors. Its formaldehyde-addition product, dimethylolnitramide, I, is however, more stable. Thus, although nitramide decomposes at 20° C. in very dilute acid, addition of formaldehyde, especially in excess, retards its decomposition for days in 10 to 20% nitric acid. Dimethylolnitramide is thus represented as the DPT precursor. This assumption, as well as the related postulate that a formaldehyde-ammonia mixture is an equilibrium source of methylenediamine does of course require further experimental support.

This support is furnished, in part, by several analogous reactions. Thus when the nitramide-formalin solution is allowed to stand overnight with a slight excess of ethylenediamine at 0° C. a compound is formed which has the composition of 3,7-dinitro-1,5-*endo*-ethylene-1,3,5,7-tetrazacyclooctane. This *homo*-DPT, III, resembles DPT closely in properties. Decomposition with 5% sulphuric acid gives the requisite amounts of formaldehyde and ethylenediamine on distillation (6). This verifies the hypothesis that a diamine tends

TABLE II
PREPARATION OF DPT FROM NITRAMIDE

Expt. No.	First solution		Nature	Second solution		Total methylene nitramide from all ingredients	DPT		Remarks
	Nitra- mide, mole	CH ₂ O, mole		NH ₃ , mole	CH ₂ O, mole		Yld., %	M.p., °C.	
*1	0.0015	0.0015	10% ammonia	—	—	1/1	22	203	Neut. to pH 6.5
2	0.001	0.006	10% ammonia	—	—	6/1	73	200	Neut. to pH 6
3	0.001	0.001	10% ammonia -formalde- hyde	0.001	0.0015	2.5/1	48	201	Fresh ammonia- formalin used.
4	0.001	0.001	Aqueous hexamine	0.010	0.015	16/1	0	—	
5	0.001	0.001	CH ₂ O - 10% NH ₃ - water. Solution aged 3 hr.	0.001	0.0015	2.5/1	0	—	Addition of more NH ₃ after 1 hr. gave 24% DPT
6	0.001	0.001	Henry solution	0.0015	0.0015	2.5/1	54	204	
7	0.001	0.001	Hexamine- ammonia	0.0027	0.0015	2.5/1	11	201	
*8	0.0032	0.0032	Methylene- diamine sulphate	0.0032	0.0016	1.5/1	60	204	Solution neutral- ized with Na ₂ CO ₃ to pH 7 at end
9	0.0016	0.004	Ditto	0.0024	0.0012	3.2/1	63	203	Ditto
10	0.002	0.004	Ditto	0.0026	0.0013	2.6/1	62	204	Ditto
11	0.0010	0.006	Ditto	0.0020	0.001	7/1	78	205	Ditto
12	0.0016	0.004	Ditto	0.0024	0.0012	3.2/1	49	204	Sulphate neutral- ized prior to ad- dition
13	0.001	0.003	10% ammonia	—	—	3.0/1	48	199-200	Neut. to pH 6.5 with NH ₃

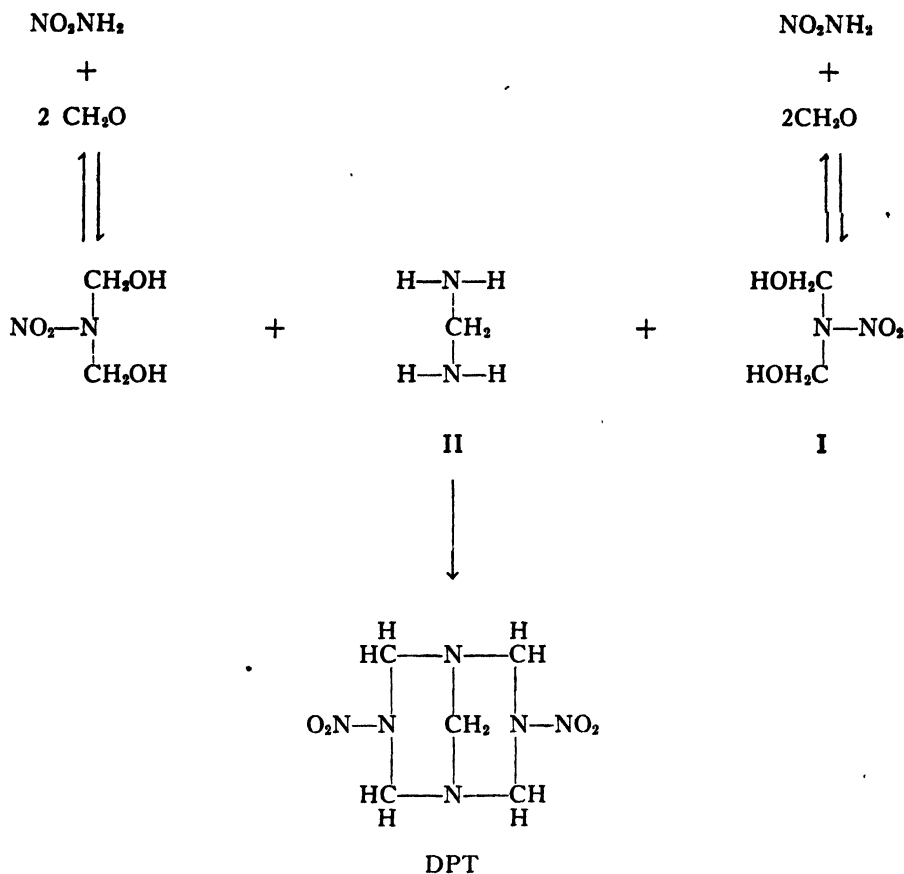
* Excess nitramide was used in these reactions, so yield was calculated on total methylene basis.

to condense with two molecules of dimethylnitramide to form a bridged eight-membered ring. It follows from this hypothesis that a mono-amine ought to form an unbridged eight-membered ring.

This was found to be the case when methylamine was treated at 0° C. with an excess of the formaldehyde-nitramide solution. The precipitate, 1,5-dimethyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IV, was not very stable but was identified by analyses, molecular weight determination, and by quantitative decomposition to formaldehyde and methylamine.

It should be noted that this unbridged eight-ring forms even though an excess of formaldehyde is present. The excess of formaldehyde might have

been expected to form, with methylamine, N,N-dimethylmethylenediamine by analogy with the presumption that formaldehyde and ammonia form methylenediamine, II, in the DPT synthesis. Such is evidently not the case; yet one might expect that certain amines would behave in this manner.



Actually we have found that cyclohexylamine acts in this manner. When 10% aqueous cyclohexylamine is added to an excess of dimethylolnitramide-formaldehyde solution at 0° C., an 80% crude yield of 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII, is formed in fair purity. This structure was allocated because of elemental analysis, molecular weight determination, quantitative formaldehyde estimation, and identification of cyclohexylamine, as its picrate, in the decomposition distillate. The compound is unstable in hot solvents.

The ease with which 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII, can be formed from cyclohexylamine, formaldehyde, and dimethylolnitramide, I, suggested its use for confirmation of the existence of I in the Hale reaction liquors. A portion of the liquor which was chosen precipitated 23% (per mole of hexamine) of the theoretical amount of DPT. The remainder of this liquor was neutralized until the free acid content was about 1%; a single extraction with cold ether removed about half the dimethylolnitramide, since

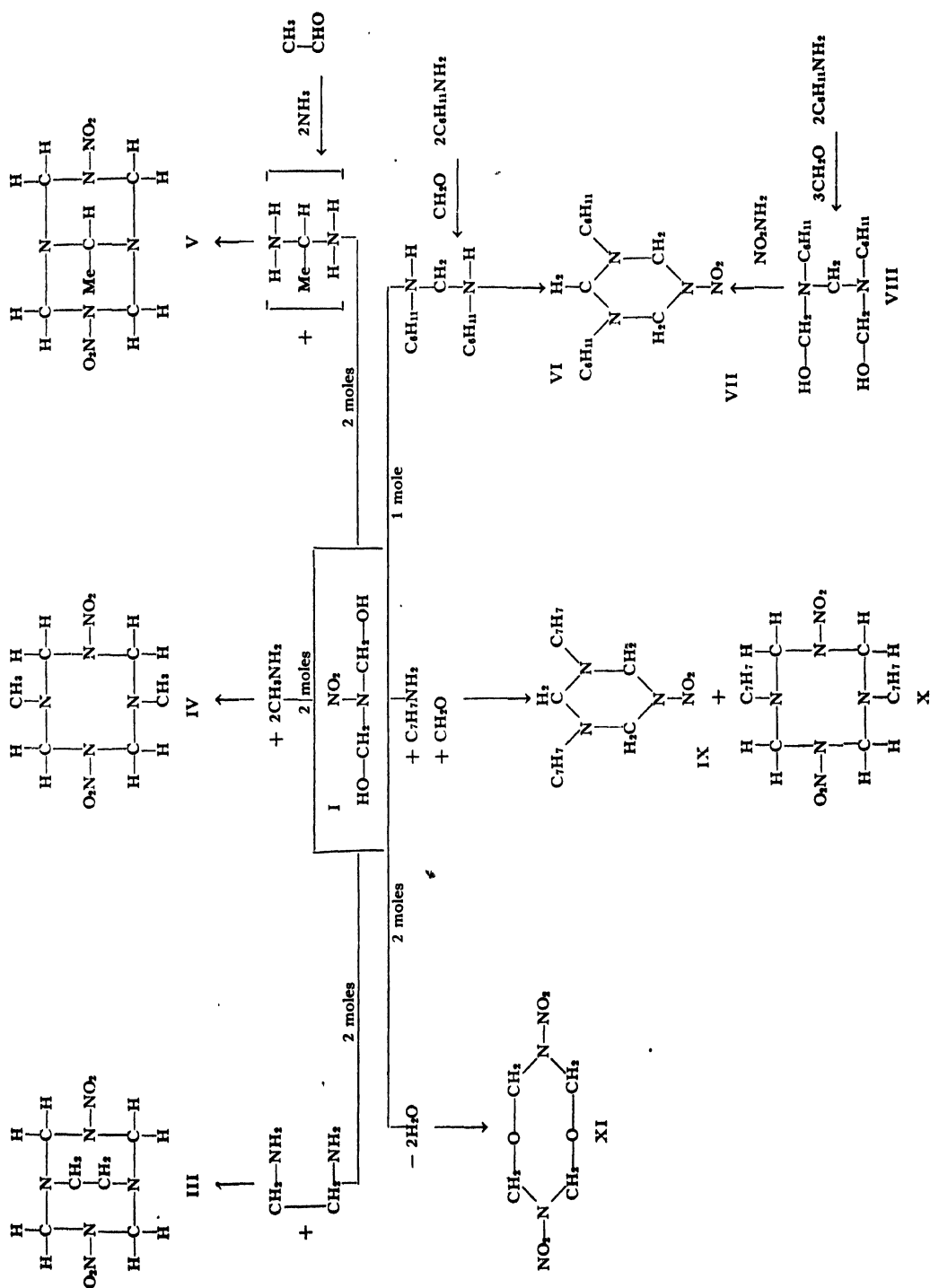
the remaining half could be precipitated as DPT by neutralization of the 1% acid solution with ammonia. The ether extract was evaporated over a water phase, which yielded VII when it was treated with cyclohexylamine. The yield of VII was 70% of that expected on the basis of the yields of DPT.

The transfer of dimethylolnitramide from the Hale reaction liquor by ether extraction is necessary when 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII, is used for its characterization because the formation of DPT is much more rapid than that of VII. Ammonium nitrate is always present in Hale reaction liquors, and its neutralization by a base such as cyclohexylamine will furnish the ammonia required for DPT synthesis.

It should be mentioned that this characterization of dimethylolnitramide depends on the assumption that cyclohexylamine and formaldehyde react to form methylene-*bis*-cyclohexylamine, VI. A precipitate, indeed, is formed when cyclohexylamine is added to formalin, but this compound has not been identified. It could, instead of VI, be N,N'-dimethylol-N,N'-dicyclohexyldiaminomethane, VIII, in which case nitramide alone would complete the reaction to form 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII. While either nitramide or dimethylolnitramide would be extractable by ether from the Hale liquors it is highly questionable that free nitramide could exist more than momentarily in the acidic solution.

Nevertheless one should realize that if dimethylolnitramide, I, exists it evidently is in equilibrium with formaldehyde and nitramide. Thus, the addition of ammonia alone to a solution of two moles of formaldehyde and one mole of nitramide causes formation of a 35% yield of DPT. It is obvious in this case that part of the formaldehyde needed to form methylenediamine, II, must have come from I, or from incomplete reaction of the nitramide and ammonia which were combined stoichiometrically to form I. The equilibrium must, however, lie far in the direction of the dimethylolnitramide. This is evident in the fact that an ether extract of the Hale reaction liquors is not altered by treatment with aqueous sodium bisulphite. The formaldehyde-bisulphite complex is not formed nor is nitramide freed by this treatment.

Since dimethylolnitramide must nevertheless exist in equilibrium with formaldehyde and nitramide, one cannot say unequivocally that 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII, is formed from dimethylolnitramide. The formation of the six-membered ring in VII could arise either from VI or VIII, and the latter bears a slight formal resemblance to the known hydrobenzamide. The formation of a compound containing an eight-membered rather than a six-membered ring would, however, favor that path whereby dimethylolnitramide was an intermediate, because nitramide in this event would have to react with an aliphatic dimethylolamine, and compounds of this type are unknown. In particular benzylamine does not form a dimethylol compound.

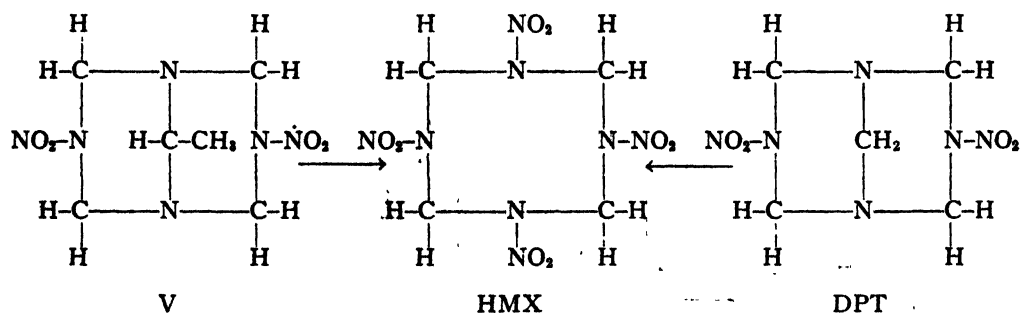


One mole of benzylamine does, however, condense with two moles of nitramide and 12 moles of formaldehyde and in this instance gives a mixture of the six- and eight-membered ring compounds, IX, 1-nitro-3,5-dibenzyl-1,3,5-triazacyclohexane and X, 1,5-dibenzyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane. Although the compounds were identified only by analysis, no reasonable alternatives involving these empirical formulae could be devised. The formation of these compounds affords further proof that dimethylnitramide is the reaction intermediate.

Among the reactions outlined thus far in this series, only formaldehyde has been used. The integrity of dimethylnitramide might be substantiated if, on addition of another aldehyde, a tetrazacyclooctane ring containing only methylene groups was obtained. Six moles of acetaldehyde were used to test this possibility, and they did not alone react with two moles of nitramide, because no precipitate was obtained when ammonia was added to neutrality of pH 7. However, when four moles of formaldehyde were then added, a precipitate appeared which, according to analysis, could be 1,5-*endo*ethylidene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, V. Like the other bridged eight-membered ring compounds DPT and 3,7-dinitro-1,5-*endo*ethylene-1,3,5,7-tetrazacyclooctane, III, it was thermally more stable than the unbridged compounds. If V is the correct structure, then two moles of dimethylnitramide must have reacted with the complex ethylenediamine.

The structure of V was confirmed by nitrolysis at 0° C. with 50 moles of 99% nitric acid. A mixture of compounds was obtained, from which a 22% yield of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) could be separated, probably from 2-methyl-1,3,5-trinitro-1,3,5-triazacyclohexane, although the latter was not identified. The isolation of the tetranitro compound locates the methyl group on the ethylidene bridge, and hence substantiates the mechanism proposed for formation of V.

The tetranitrotetrazacyclooctane, which has been symbolized as HMX (high-melting explosive) in the following formulation, is a new compound,



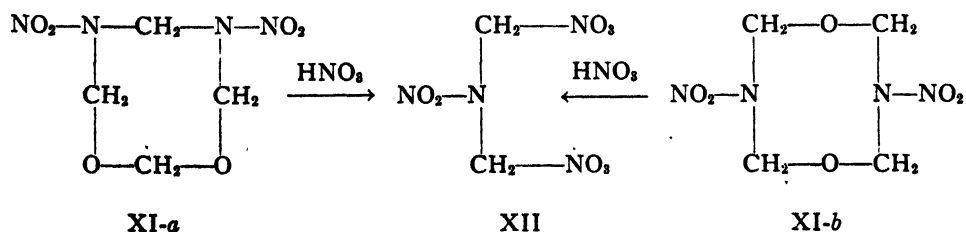
the tetramer corresponding to Cyclonite as the trimer of the hypothetical methylenenitramine. It is also obtained, in trace, in the Hale nitrolysis of hexamine, and in 34% yield by the nitrolysis of DPT where, again, the bridge is removed. Its constitution was established by Bachmann (1) by molecular weight determination.

While the condensation reactions outlined above support the existence of dimethylolnitramide, the best proof of its existence was obtained by a dehydration experiment where the formalin-nitramide solution was evaporated to dryness and heated *in vacuo* at 100° C. The residue, after purification, constituted a 16% yield of 3,7-dinitro-3,7-diaza-1,5-dioxacycloöctane, XI, and thus is the dehydration product arising by removal of two molecules of water from two molecules of dimethylolnitramide.

The reliability of this proof depends of course, on the constitution of XI. This compound had been prepared by Whitmore and Noll (8) by the action of nitric acid - ammonium nitrate mixture on hexamine dinitrate for 168 hr. When their preparation was repeated, a 16% yield of compound XI could be filtered off; the filtrate after neutralization with ammonia to pH 6.5 slowly precipitated a 32% yield of DPT. A higher yield of DPT (39%) could be obtained after 60 hr. reaction time, but the yield of compound XI was lowered to 11%. This suggests that the initial reaction involves the formation of dimethylolnitramide from hexamine dinitrate (two moles per mole, and this is the yield basis). The dimethylolnitramide thus produced quite rapidly (DPT yield was 23% after one hour reaction) is either stabilized by slow dehydration to XI or decomposes slowly over the 168 hr. period. The presence of dimethylolnitramide was demonstrated further by neutralizing an aliquot with sodium carbonate to pH 2, extracting the solution with ether, evaporating the ether solution with water, and then adding cyclohexylamine. The precipitate which formed was 1-nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII.

A modification of this experiment proved that DPT was unstable in nitric acid and probably decomposed to dimethylolnitramide. When DPT was allowed to stand 11 days in nitric acid - ammonium nitrate solution, dilution with water precipitated XI in 12% yield on the equimolar basis. Neutralization of the filtrate to pH 6.5 returned 44% of the DPT, evidently by resynthesis from dimethylolnitramide which had not decomposed during the 11 day period at 11° C.

The preparation of 3,7-dinitro-3,7-diaza-1,5-dioxacycloöctane, XI, is therefore a modification of the dehydration by which the existence of dimethylolnitramide was to have been proved. In order to support the case for dimethylolnitramide, further proof of structure for XI was necessary, and this was provided by nitrolysis. The structural possibilities for a nitramine having this empirical formula are limited, but two, XI-a and XI-b can be written:



Both of these compounds could give dinitroxydimethylnitramide, XII, by nitrolysis with nitric acid, but only one, XI-*b*, could give two moles of XII. When one mole of XI is treated with 20 moles of nitric acid at 5° C. for 14 min. and then drowned in water, a yield of XII was obtained which was 68% on the basis XI-*b*→XII but would have been greater than theoretical on the basis XI-*a*→XII. The structure of XI (as XI-*b*) is thus established, and with it the identity of dimethylolnitramide if XII has the structure assigned to it.

Dinitroxydimethylnitramide, XII, is a very unstable solid in humid air but it will survive several days in a dry environment. It can be converted in 68% yield to the more stable diacetoxydimethylnitramide, XIII, by short boiling with a sodium acetate solution in acetic acid. In fact the two derivatives are interconvertible, since the liquid XIII can be converted in 38% yield to the solid XII by treatment at 5° C., with 20 moles of nitric acid. The interconvertibility of these two simple compounds establishes the constitution of each beyond a reasonable doubt, and therefore establishes the entire series of reactions which have been outlined in this report.

Experiments with dinitroxydimethylnitramide, XII, indicate that the compound is only slightly soluble in 15 to 20% nitric acid, and is fairly unstable in nitric acid medium. Thus, when a mole of XII is treated at 20° C. for 25 min. with 20 moles of 99% nitric acid and then drowned in ice-water to a nitric acid concentration of 20%, there is reprecipitated 50% of the original XII. Neutralization of the filtrate to pH 6.5 with ammonia accounts for only 2% more as DPT. This experiment indicates that some dinitroxydimethylnitramide may be precipitated with the RDX in a Hale reaction. Certainly crude RDX contains unstable impurities which must be destroyed by boiling. The experiment also explains the decrease in DPT yield (upon ammonia neutralization) with increasing age of undiluted Hale reaction liquors (Table I). It suggests that XII may be a major product of hexamine nitrolysis, despite the fact that only 10 to 20% of DPT can be obtained upon neutralization.

This argument is erroneous to the extent that the crude yield of Cyclonite is only about 4% higher than the refined yield whereas inclusion of half the dinitroxydimethylnitramide into the crude Cyclonite (if XII were produced on a 1 : 1 basis with Cyclonite) should increase the crude Cyclonite yield to 50% more than the refined yield. The argument for presence of nitroxylated dimethylolnitramide, XII, in the Hale dilution liquors is also weakened by the observation that XII is hydrolyzed quite slowly (nine hours) under the conditions of DPT formation, although a 60% yield of the latter compound is eventually obtained. This discrepancy in neutralization time, may, however, not be significant, since in this experiment the system was heterogeneous, and was maintained at a higher pH (8 to 9) than is ordinarily customary for DPT formation.

These considerations indicate that dimethylolnitramide may be present wholly or partly in the unesterified form in undiluted Hale reaction liquors. Its stability is sufficient to warrant this conclusion. When a cold aqueous

solution of dimethylolnitramide is fortified with absolute nitric acid to 90% HNO_3 concentration and is held at 20° C. for two minutes before dilution, a 58% yield of DPT results on neutralization. If the solution is held 30 min. before dilution, the DPT yield is 15%, and this yield agrees closely with that obtained by neutralizing a Hale reaction liquor of about 30 min. age in the undiluted state.

Whether dimethylolnitramide is present in the esterified form or otherwise, it seems reasonable to presume that it originates in appreciable yield as a product of the Hale nitrolysis.

Experimental*

DPT from Nitrolysis of Hexamine

The revised Hale procedure is as follows. A three-necked flask is equipped with thermometer, stirrer, and a helical hexamine feeder built around a motor-rotated Irwin bit. The 500 cc. flask contains 133 gm. (2.1 moles) of vigorously stirred 99.6% nitric acid maintained at 20° to 25° C. (with an ice-salt bath.). The finely powdered hexamine (14 gm., 0.1 mole) is introduced through the solids feeder over 12 to 15 min. at a uniform rate so as to avoid local decomposition, and, sometimes, fire at the acid interface. The rate is difficult to maintain in a glass vessel because of a large heat of reaction, and stainless steel or aluminum has sometimes been used. When a glass vessel is used, it is convenient to use hexamine dinitrate instead of the amine, the quantity of nitric acid being adjusted accordingly. The slurry is allowed to age from 5 to 15 min., depending on the reaction temperature, and is then poured into 1 kilo of ice. This is much safer than the reverse dilution where ice and water are added gradually to the chilled slurry at -10° C., because a violent decomposition frequently occurs when partial dilution has reached an acid concentration of about 70 to 75%. The fresh, undiluted reaction slurry is stable even in the presence of catalyzing nitrogen peroxide, but this stability decreases (with increasing formaldehyde-like odor) with age so that, after one day, fume-off invariably results spontaneously or by introduction of nitrogen peroxide. No Cyclonite is destroyed by this fume-off.

The cold filtrate from which the Cyclonite has been removed is stirred and chilled while 15 to 25% ammonia is added slowly. No precipitate appears until the solution reaches pH 5.4 to 5.6, and it then forms slowly; ammonia must be added cautiously (colorless gas is evolved if pH 7 is exceeded) to compensate an increasing acidity. After pH 6.5 has been maintained over 10 to 15 min., the precipitate is filtered off and the filtrate further neutralized cautiously to pH 7 to determine completeness of precipitation. The yield of DPT, m.p. 177° to 199° C., varies from 1.1 to 2.6 gm. under these reaction conditions or 5 to 12% of theoretical on the basis of one mole from one mole of hexamine.

* All melting points corrected against reliable standards.

DPT from Hexamine Dinitrate and Acetic Anhydride

A mixture of 1940 cc. (20 moles) of acetic anhydride and 1330 gm. (five moles) of hexamine dinitrate was stirred for two to three days. The initial temperature increase subsided after a few hours. The slurry was then filtered and water-washed to remove 224 gm. of pure DPT melting at 205° to 206° C. The filtrate was drowned to 10% acetic acid concentration and a further 109 gm. was obtained, m.p. 187° to 200° C. The total yield was 30.6% of theoretical. A longer or shorter reaction period gave lower yields and inferior product. Neutralization of the final aqueous precipitate yielded no further product.

DPT may be crystallized from acetone, ethyl acetate, nitromethane, dioxane, or from acetic anhydride. It is soluble in acetic acid, and gives a positive Franchimont test. Calc. for $C_6H_{10}N_6O_4$: C, 27.5; H, 4.63; N, 38.5%. Found: C, 27.7; H, 4.58; N, 38.9%.

Although the compound is unstable in aqueous acid, its partial recovery by neutralization demonstrates a basic amino group. A solution of 0.5 gm. DPT in 10 to 15 cc. concentrated hydrochloric acid at 10° C. yielded on neutralization with alkali after 15 min. a 58 to 46% recovery, depending on the amount of acid used. The precipitation was complete at pH 3.4. The behavior in nitric and sulphuric acids showed greater decomposition. A 45% recovery (first appearing at pH 5.6) was effected by solution of 0.5 gm. DPT in 25 cc. of 40% nitric at 0° to 20° C., if neutralization was immediate. After 45 min. only 34% could be recovered. When stronger nitric acid was used (70 to 95% at 0° to 8° C.) the recovery of DPT (appearing at pH 5.6) was 12%. When 0.5 gm. of DPT was dissolved in 40 cc. of 40% sulphuric acid at 0° to 5° C., neutralization with ammonia after 15 min. gave a 36% recovery, initially at pH 5.0, but only 15% could be recovered from 90% sulphuric acid; the suspension gassed strongly. However, an 82% recovery at pH 5.6 could be effected from 22 gm. of DPT in 40 cc. of 86% sulphuric acid; this was partly owing to incomplete solubility, but there was no gas evolution.

DPT from Hexamine Dinitrate and Sulphuric Acid

One-tenth mole of hexamine dinitrate was added proportionately with 0.92 mole of 90% aqueous sulphuric acid to a stirred flask at 8° to 15° C. over a 30 min. period. After 45 min. subsequent stirring at 14° to 15° C., the mixture was poured into 400 cc. of ice and water. The solution was almost clear, but was filtered and neutralized to pH 5.6 to 6.5 with 28% ammonia to yield 0.031 mole (31% of theory) of DPT, m.p. 199° to 201° C. This yield was decreased to 23% when the addition time was 13 min., with seven minutes' subsequent stirring.

The yield could be increased to 35% by adding the two ingredients proportionately to 0.2 mole of 98 to 99% nitric acid; but in this case a 14.5% yield of impure Cyclonite (m.p. 188° to 198° C.) had to be filtered off before neutralization.

DPT from Dimethylolnitramide and Formaldehyde-Ammonia

To 0.48 cc. (0.006 mole) of 37% formalin solution which was cooled to 0° C. was added, with cooling, 0.25 gm. (0.004 mole) of freshly prepared nitramide (2). There was no apparent heat of solution. After dilution with 2 cc. water a 10% aqueous solution of ammonia was added dropwise with cooling until a pH of 7 was reached. The precipitate formed slowly over a five minute period but was allowed to stand in the mother liquor for 40 min. at 0° C. The product weighed 0.215 gm. after filtration, water wash, and drying at 50° C. The yield, m.p. 206° to 208° C. (decomp.), was 83% on the formaldehyde basis.

DPT from Dimethylolnitramide and Methylenediamine

The methylenediamine was prepared according to Knudsen (5) but the analysis of our acid salt gave a methylenediamine:sulphuric acid ratio of 5:6 while he suggests a ratio of 3:4. The salt was always analyzed before use.

To a cold nitramide-formaldehyde solution, prepared by mixing 0.10 gm. (0.0016 mole) of nitramide and 0.12 cc. (0.0016 mole) of 37% formalin as outlined above, was added 0.20 gm. (0.0011 mole) of methylenediamine sulphate together with 7.5 cc. water to dissolve this salt. The resulting solution was cooled to 0° C. and neutralized to pH 7 with saturated aqueous carbonate. The white precipitate which appeared at once was filtered after 40 min., washed with 10 cc. water, and dried at 50° C. The product weighed 0.085 gm. (97% CH₂O basis) and melted at 206° to 208° C. (decomp.).

The instability of the methylenediamine in aqueous solution is attested by the fact that a lower yield was obtained if the methylenediamine sulphate was neutralized with sodium carbonate before it was added to the nitramide-formaldehyde solution.

It might be argued that the instability of methylenediamine would augment the formaldehyde-ammonia content of the solution to such an extent that the yield of 97% in experiment would be invalidated. Actually it would be calculable as 73% if all the methylenediamine had decomposed to formaldehyde and ammonia. Under any circumstances, such a reservation is not tenable because of the rapidity of the reaction to form DPT when methylenediamine is employed, as contrasted to the use of formaldehyde-ammonia.

Furthermore the enhancement of yield using methylenediamine can be shown when other ratios and excesses are used. Thus, inspection of Table II shows that when formaldehyde and ammonia alone are used with nitramide, the yield of DPT increases from 22% to 48% (methylene basis) as the methylene-nitramide ratio increases from 1:1 to 2.5:1. A ratio of 1.5:1 will therefore produce a yield between these limits when formaldehyde-ammonia is used, but this ratio (Expt. 8) produces a 60% yield (methylene basis) when part of the methylene is in the form of methylenediamine.

Again, when methylene is in excess and the yield is calculated on the nitramide basis, a 3 : 1 ratio of methylene to nitramide yields 48% of DPT when formaldehyde and ammonia are used (Expt. 13) and this is practically the same if a previously neutralized methylenediamine sulphate solution is used (Expt. 12), but yields of 62 to 63% are obtained at ratios of 3.2–2.6 : 1 if the methylenediamine is freed from its salt *in situ*.

Stability of Dimethylolnitramide in Nitric Acid

Dimethylolnitramide was prepared in the usual way by mixing 0.11 gm. (0.0018 mole) of nitramide and 0.32 cc. (0.0043 mole) of formalin (37%) with cooling. The solution was cooled in a dry-ice bath while a solution of 0.14 gm. (0.0018 mole) of ammonium nitrate in 2.5 gm. (0.039 mole) of 99% nitric acid was added to it. If the resulting solution (C) were allowed to warm to 10° C. over a two minute period and was then drowned in 9 gm. ice–water mixture, a 46% yield (formaldehyde basis) of DPT was obtained when the solution was neutralized with ammonia. If, on the other hand, the solution (C) were allowed to stand at 20° to 25° C. for 30 min., the yield of DPT was only 15%.

Dimethylolnitramide is evidently more stable in dilute (10 to 20%) nitric acid than in the absolute acid, since a Hale filtrate (12% HNO₃ content) gave a 21% yield of DPT on the day the nitration was carried out; this decreased to 14% after seven days, and no DPT was obtained after 20 days.

3,7-Dinitro-1,5-endoethylene-1,3,5,7-tetrazacyclooctane, III

A cold solution of 0.62 gm. (0.01 mole) of nitramide in 3.0 cc. (0.04 mole) of 37% formalin was treated at 0° C. with 3.3 cc. (0.0055 mole) of 10% ethylenediamine solution plus 5 cc. water. After 12 hr. the precipitate which formed slowly was filtered off, water-washed, and dried at 50° C. It weighed 0.52 gm. (45% theory, nitramide basis) and melted at 134° to 139° C. with violent frothing.

This compound has much the same properties as its homologue, DPT. It is insoluble in warm ethanol, benzene, dioxane, methanol, acetic acid, and carbon tetrachloride but soluble in warm acetone and warm nitromethane. It is decomposed readily in boiling nitromethane and boiling water with evolution of formaldehyde. The pure compound is obtained in short, distinct needles by crystallization from warm acetone, m.p. 140° C. (frothing). Calc. for C₁₈H₁₂N₆O₄: C, 31.0; H, 5.21; N, 36.2%. Found: C, 30.6; H, 5.24; N, 35.7%. Hydrolysis with 5% sulphuric acid gave formaldehyde and ethylenediamine; the latter was obtained as its picrate after neutralization of the alkali distilled hydrolyzate. Both fragments were estimated quantitatively (6). Calc. for CH₂O, 51.7; ethylenediamine, 25.9%. Found CH₂O, 52.7; ethylenediamine, 26.3%.

1,5-Dimethyl-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IV.

To a cold solution made by dissolving 1.50 gm. (0.024 mole) of nitramide in 12 cc. (0.16 mole) of 37% formalin was added 3.6 cc. (0.012 mole) of 10%

methylamine solution with stirring. A dense precipitate formed at once. The reaction mixture was aged 15 min. longer at 0° C. and then filtered; the precipitate was washed with 125 cc. water and dried at 50° C. It weighed 0.62 gm. (44% on methylamine basis) and melted at 124° C. (decomp.):

The substance IV is soluble in acetone, ethanol, chloroform, and 10% aqueous sodium hydroxide but is insoluble in petroleum ether and diethyl ether. It is unstable in hot solvents and deteriorates by exposure to moist air. It may be purified by crystallization from acetone (25° C. to -40° C.) as needles, m.p. 124° C. Its molecular weight by the Barger-Rast method in acetone was found as 243 (calc. 234). Calc. for $C_{16}H_{14}N_6O_4$: C, 30.7; H, 6.02; N, 35.9%. Found: C, 30.9; H, 6.01; N, 36.4%. Methylamine was identified as its picrate in the distillate from which the compound was hydrolyzed in aqueous solution. The compound was analyzed quantitatively for methylamine and formaldehyde. Calc. for $C_6H_{14}N_6O_4$: $4CH_2O$, 51.3; $2CH_3NH_2$, 26.5%. Found: $4CH_2O$, 53.2; $2CH_3NH_2$, 31.0%.

1-Nitro-3,5-dicyclohexyl-1,3,5-triazacyclohexane, VII.

A solution (10 cc., 0.01 mole) of 10% aqueous cyclohexylamine was added with stirring to a cooled solution of 1.24 gm. (0.02 mole) of nitramide in 9.0 cc. (0.12 mole) of 37% formalin. A very dense white precipitate formed immediately and was filtered off after the slurry had aged 15 min. at 0° C. After washing with 25 cc. of water, it was dried at 50° C. It weighed 1.20 gm., m.p. 94° to 96° C. (decomp.), a yield 80% of theoretical on the cyclohexylamine basis.

The compound VII is slightly soluble in cold ethanol, methanol, chloroform and is very soluble in cold benzene, acetone, dioxane, glacial acetic acid, and methyl ethyl ketone. It is unstable in hot solvents and is best kept over phosphorus pentoxide. It crystallizes as flakes from acetone (25° → 0° C.) with melting point, pure, of 99° C. Its molecular weight (Barger-Rast in acetone) was found as 290 (calc. 296). Calc. for $C_{16}H_{28}N_4O_2$: C, 60.8; H, 9.49; N, 18.9; CH_2O , 30.4%. Found: C, 60.4; H, 9.43; N, 18.8; CH_2O , 31.9%. Hydrolysis in dilute alkali resulted in evolution of cyclohexylamine, identified as its picrate, in the distillate.

Dimethylolnitramide with Benzylamine-Formaldehyde

To a cold solution of 0.124 gm. (0.002 mole) of nitramide in 0.90 cc. (0.012 mole) of 37% formalin was added with shaking 1.07 cc. (0.001 mole) of 10% aqueous solution of benzylamine. A dense white precipitate formed immediately and, after the slurry was digested at 0° C. for 20 min., the precipitate was filtered, washed with 30 cc. of water, and dried at 50° C. The weight of product was 0.095 gm., m.p. 93° to 95° C. (frothing).

This crude mixture is insoluble in ethanol, soluble in cold ethyl acetate and benzene, and very soluble in cold acetone and methyl ethyl ketone. It decomposes in hot solvents. The two constituents were separated by dissolving the crude in a minimum of acetone at 25° C. cooling to 0° C. The eight-membered

ring compound, X, separated out leaving the six-membered ring compound, IX, in solution. The latter was recovered by 1:1 dilution of the filtered liquor with water.

The melting point of dibenzyl dinitrotetrazacyclooctane, X, is 150.5° C. (decomp.) after crystallization, in fluffy needles, from acetone. Calc. for $C_{18}H_{22}N_8O_4$: C, 55.9; H, 5.75; N, 21.7%. Found: C, 56.1; H, 5.67; N, 21.7%.

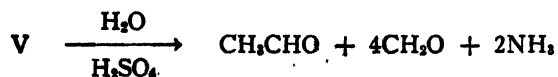
Nitrodibenzyl triazacyclohexane, IX, is purified in a fluffy, noncrystalline form by precipitation from acetone with water to melt at 109° C. Calc. for $C_{17}H_{16}N_4O_2$: C, 65.3; H, 6.47; N, 17.9%. Found: C, 65.4; H, 6.38; N, 17.9%.

1,5-Endoethylidene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, V.

A solution of 0.124 gm. (0.002 mole) of nitramide in 2.75 cc. (0.012 mole) of 20% acetaldehyde was cooled by ice bath while 0.56 cc. (0.003 mole) of 10% ammonia was added. After 20 min. digestion at 0° C., 0.30 cc. (0.004 mole) of 37% formalin was added. Since precipitation was slow, the mixture was maintained at 0° C. for two hours, then filtered, and the crystalline product washed with water and dried at 50° C. The product weighed 0.090 gm. (30% of theoretical on formaldehyde basis) and melted at 173° C. (shrinkage with residue finally melting at 245° C.).

This compound is insoluble in hot benzene, ethanol, acetic acid, chloroform, and dioxane but slightly soluble in warm acetone and methyl ethyl ketone. It was purified from warm ethyl acetate to give small well defined crystals, m.p. 175° C. with a brown residue remaining up to 245° C. Calc. for $C_8H_{12}N_8O_4$: C, 31.0; H, 5.17; N, 36.2%. Found: C, 30.5; H, 5.21; N, 36.2%.

When the compound was analyzed for aldehyde and ammonia, the ratio aldehyde : ammonia of 2.44 was obtained, whereas a ratio of 2.5 might be expected according to the following equation:



1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane, HMX

When 2.18 gm. (0.01 mole) of DPT was added to 12.7 gm. (0.2 mole) of 99.6% nitric acid at 0° to 10° C. over five minutes, a slurry formed. After 25 min. this mixture, drowned in ice, yielded a precipitate melting at 232° to 260° C. This was heated with 70% nitric acid until nitrogen oxides were evolved, then cooled, chilled, and filtered. The washed, dried material weighed 1.01 gm. or 34% of theoretical and melted at 278.5° to 279.5° C. Recrystallization from acetone, 70% nitric acid, dioxane (10% solution hot, 9% solution cold) or nitromethane, (solution 7.5% hot, 2.2% cold) raised this to 280.0° C. (decomp.). These solubilities refer to crystallization over a few hours; the acetone solution precipitates more HMX over several days.

The solubility of HMX in pyridine is limited and this probably accounts for a low molecular weight value (250) in this solvent by the isopiestic Barger-Rast method. Calc. for $C_4H_8N_8O_8$: C, 16.22; H, 2.72; N, 37.8%. Found: C, 16.4; H, 2.76; N, 38.2%.

The molecular weight was determined ebullioscopically by Bachmann as 296. The crystallization from nitromethane yields initially a needle-shaped polymorph which converts to a massive form on reheating.

HMX was also prepared from 1,5-endoethylidene-3,7-dinitro-1,3,5,7-tetraazacyclooctane, V, when 0.52 gm. (0.0024 mole) m.p. 236° to 245° C., was added over a period of 11 min. to 4.75 cc. (0.112 mole) of 99% nitric acid at 0° C. The resulting solution was digested 50 min. longer at 0° C. and then drowned in 150 cc. of ice-water mixture, the precipitate filtered, washed with water, and dried at 50° C. Weight was 0.27 gm., m.p. 179° to 184° C. (decomp.). This was separated by several crystallizations from warm ethyl acetate into 0.15 gm. of impure HMX, m.p. 261° to 271° C. Yield of HMX was 22% of theory (1 : 1 mole basis). The remainder of the crude nitration product was for the most part HMX contaminated with some impurity, probably 2-methyl-1,3,5-trinitro-1,3,5-triazacyclohexane.

3,7-Dinitro-3,7-diaza-1,5-dioxacyclooctane, XI

A. From Dimethylolnitramide

A cold solution of 0.62 gm. (0.01 mole) of freshly prepared nitramide in 1.50 cc. (0.02 mole) of 40% formalin was allowed to stand at 0° C. for five minutes and then immersed in a 60° C. water bath and evaporated to dryness under reduced pressure (12 mm.). After most of the water had been removed, a rather viscous liquid remained. The temperature of the bath was increased to 100° C. and the liquid changed to an amorphous solid which was digested at 100° C. at 12 mm. for another hour and a half and then washed with 10 cc. of water and dried at 50° C. Weight of product was 0.17 gm., m.p. 244° to 247° C. (decomp.). Yield calculated as crude XI was 16% of theory on a 2 : 1 basis. One crystallization from acetone raised the melting point to 263° to 264° C. (decomp.); mixed melting point with an authentic sample (8) was not depressed.

B. From DPT

A solution of 67.2 gm. (0.84 mole) of ammonium nitrate in 55 cc. (1.31 moles) of 99% nitric acid was added rapidly to 30 gm. (0.137 mole) of DPT and the resulting slurry was warmed to 50° C. for five minutes, then cooled to 11° C. and stirred there for 11 days. At the end of this time, the reaction mixture was drowned in 250 cc. of ice-water mixture and allowed to stand overnight at 0° C. The precipitate which was filtered, water-washed, and dried at 50° C. weighed 3.35 gm., m.p. 236° to 244° C. (decomp.). Yield was 11.8% of theory (1 : 1 mole basis). One crystallization of this crude from acetone resulted in an 86% recovery of good quality material.

The drowned acid filtrate was neutralized to pH 6.5 with sodium carbonate and 13.1 gm. of crude DPT (44% of the original starting material), m.p. 180° to 182° C. (decomp.), was recovered. One crystallization of this from acetone resulted in an 86% recovery of DPT, m.p. 199° to 201° C.

C. From Hexamine Dinitrate (8)

To a solution of 643 gm. (8.04 moles) of ammonium nitrate in 530 cc. (12.5 moles) of 99% nitric acid, was added 352 gm. (1.32 moles) of hexamine dinitrate (HADN) over three minutes. The temperature of the slurry was raised by gentle warming to 42° to 45° C. for 13 min., cooled to 7° C., and the thick sludge stirred for seven days at this temperature, then drowned in three liters of ice-water mixture and allowed to stand at 0° C. for two days. The crystalline precipitate was filtered, water-washed, and dried at 50° C. Weight of XI was 43.5 gm., m.p. 262° to 264° C. (decomp.). The acid filtrate was neutralized to pH 6.5 at 5° C. with 28% ammonia and 110 gm. of DPT, m.p. 190° to 192° C. (decomp.) was obtained. Yield of crude DPT was 38% on the basis of one mole of HADN giving one mole of DPT. The yield of XI was 16% of theory on the basis of one mole of XI from one mole of HADN.

Dinitroxydimethylnitramide, XII, from XI

To 25.6 cc. (0.58 mole) of 99% nitric acid at 5° C. was added 6 gm. (0.0288 mole) of XI over seven minutes. The resulting solution was aged seven minutes longer at 0° C.; and then drowned in 200 cc. of ice-water mixture. The slightly lumpy precipitate was filtered after standing 10 min. at 0° C., ground in a mortar, washed acid-free with water, and dried at 25° C. *in vacuo* over phosphorus pentoxide. Weight of the product was 8.30 gm., m.p. 58° to 60° C. Yield calculated as crude dinitroxydimethylnitramide was 68.3% of theory (on basis of one mole of XI giving two moles of XII.).

The compound is soluble in methanol, ether, ethyl acetate, acetone, nitromethane, and dioxane. It is slightly soluble in benzene and chloroform and insoluble in water. It can be purified by crystallizing from warm ether in wedge-shaped crystals, melting at 59° to 60° C. It decomposes readily on standing exposed to the air, but can be stored for several days, without decomposition, *in vacuo*. It is a powerful impact-sensitive explosive. Calc. for $C_2H_4N_4O_8$: C, 11.3; H, 1.89; N, 26.4%. Found: C, 11.4; H, 1.89; N, 26.3%.

Diacetoxydimethylnitramide, XIII, from XII

To a solution of 23.9 gm. (0.292 mole) of anhydrous sodium acetate in 120 cc. (2 moles) of acetic acid at 35° C. was added 15.5 gm. (0.0731 mole) of dinitroxydimethylnitramide and the resulting suspension refluxed for three minutes. The reaction mixture was then cooled to 30° C. and the acetic acid removed under reduced pressure. The residue from this distillation was extracted with two portions of 250 cc. of ether and finally with 200 cc. of ether. The ether was removed from the ether extract with a stream of dry air and the resulting residue was distilled under reduced pressure to remove further

traces of acetic acid. The oily residue which remained was suspended in 20 cc. of water, neutralized to pH 9 with sodium carbonate, and the diacetate was extracted with four 60 cc. portions of ether. The etherous extract, which was dried over sodium sulphate, was distilled at 11 mm. pressure. The fraction boiling at 151° to 154° C., weighed 10.4 gm. Yield, calculated as crude diacetoxydimethylnitramide (XIII), was 69% of theory.

Further distillation of this fraction at 11 mm. pressure yielded a colorless liquid. The main fraction boiling at 152° to 152.7° C., (weight 5 gm.) was pure (XIII), n_D^{25} , 1.453; n_D^{20} , 1.4540; d_4^{20} , 1.311. Calc. for $C_6H_{10}N_2O_8$: C, 35.0; H, 4.86; N, 13.7%. Found: C, 35.1; H, 4.90; N, 13.9%. Molecular refraction: Calc. MR_D 43.6. Found: MR_D 42.6.

Dinitroxydimethylnitramide, XII, from XIII

To 7.3 cc. (0.171 mole) of 99% nitric acid which was cooled to 5° C. was added with stirring 1.76 gm. (0.00855 mole) of diacetoxydimethylnitramide, XIII, with swirling in an ice bath. The reaction mixture was allowed to stand 10 min. at room temperature and then drowned in 60 cc. of ice-water mixture. The precipitate was filtered, washed acid free with water, and dried at 25° C. *in vacuo*. Weight was 0.68 gm., m.p. 57° to 58° C. Mixed melting point with an authentic sample of XII was not depressed. Yield calculated as crude XII was 38% of theory (1 : 1 mole basis).

DPT from Dinitroxydimethylnitramide, XII

To a mixture of 0.208 gm. (0.001 mole) of dinitroxydimethylnitramide and 0.08 gm. (0.001 mole) of ammonium nitrate, was added a solution of 0.15 cc. (0.002 mole) of 40% formalin in 3 cc. of water. The resulting suspension was cooled in an ice bath and 10% sodium hydroxide solution was added dropwise over a period of six hours, the pH being maintained at 8 to 9, whereupon further addition of alkali was not required to maintain the pH at 8. The reaction mixture was aged three hours longer at 0° C. and the precipitate filtered. Weight of product was 65 mgm., m.p. 200° to 201° C. (decomp.). Yield calculated as DPT is 60% of theory (basis of two moles of XII giving one mole of DPT.)

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* We are indebted to Doctors Carmack, Kuehl, and Leavitt, University of Pennsylvania, for advice on applicability of this method to our compounds.

A COMPARISON OF THE DIRECT AND INDIRECT RADIOACTIVE METHODS FOR DETERMINING THE SURFACE AREA OF A STRONTIUM SULPHATE PRECIPITATE¹

R. H. SINGLETON AND J. W. T. SPINKS

Abstract

The specific surface of a strontium sulphate precipitate, as determined by the direct radioactive method using Sr^{90} , was found to be 12,800 sq. cm. per gm. The specific surface of the same strontium sulphate precipitate was also determined by the indirect method using ThB. Specific surfaces of 30,800 and 21,300 sq. cm. per gm. were obtained using ThB, separated, from thorium nitrate, by the chemical separation and emanation methods, respectively. The factor of approximately 2 between the direct and indirect methods indicates that Paneth's theories, while probably correct in the main, may require some modification.

Introduction

During the past few years the determination of surface areas of solids has become of increasing importance, and various methods for making such determinations have been developed. One method of determining the surface area of a slightly soluble inorganic crystalline precipitate depends on the occurrence of a surface exchange reaction, the extent of the exchange reaction being followed by a radioactive isotope of the cation. This method was first used by Paneth and Vorwerk (6) to determine the surface area of a finely divided precipitate of lead sulphate, using thorium B (Pb^{212}) as the radioactive indicator.* Two methods were used, the direct radioactive method and the indirect radioactive method.

The Direct Radioactive Method

When a weighed amount of lead sulphate is shaken with a saturated aqueous solution of lead sulphate containing, besides ordinary lead, some radioactive lead (e.g., ThB), a reversible kinetic interchange takes place continually between the lead ions in the surface layer of the crystal and the lead ions in solution. It is assumed that the interchange does not extend beyond the surface layer or that, if it does, the interchange with lower layers takes place relatively slowly, so that the resulting slow penetration can be distinguished from the primary surface exchange. When equilibrium has been set up, the following equation holds

$$\frac{\text{ThB in surface}}{\text{ThB in solution}} = \frac{\text{Pb in surface}}{\text{Pb in solution}} \quad (1)$$

The "ThB in solution" may be determined by centrifuging and evaporating an aliquot of the liquid and determining its activity with an electroscope (as by

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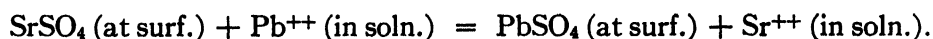
* In a recent review, Paneth (4) has suggested that the exchanging part of the surface may be smaller than the geometric surface, but at the same time the only important one for the phenomena of adsorption and catalysis and therefore well worth studying.

Paneth and Vorwerk) or with a Geiger-Müller counter. Knowing the original ThB activity, the "ThB in surface" may be calculated. The "total lead in solution" may be determined by chemical analysis and finally, using the above equation, the "total Pb in surface" may be calculated. Then, if certain simplifying assumptions are made, the surface area of the precipitate can be calculated. Paneth and Vorwerk (6) have shown that this method yields results of the same order of magnitude as the microscope method when applied to lead sulphate crystals.

It is reasonable to believe that the same method can be used with a radioactive anion tracer.

The Indirect Radioactive Method

Paneth and Thimann (3, 5) suggested that the surface area of crystalline precipitates such as barium sulphate or strontium sulphate could be determined by means of an exchange reaction similar to that just described, using a radioactive tracer which forms sulphate crystals that are isomorphic with both barium and strontium sulphate. It was known that the sulphates of barium, strontium, lead, and radium show well defined isomorphism. It was shown by Paneth that lead ions, for example, can participate in kinetic exchange with the outer layer of a precipitate of strontium sulphate. A reasonable mechanism for the exchange is:



The surface area of strontium sulphate crystals was determined using the same procedure as before except that the tracer was radioactive lead instead of radioactive strontium, the latter being unobtainable at that time. It was assumed that the individual tendencies of the lead and strontium ions to go into the crystal lattice from the solution were proportional to their respective concentrations in the aqueous saturated solution of strontium sulphate containing lead sulphate. Also, it was assumed that the individual tendencies of the lead and strontium ions to leave the lattice and go into solution were proportional to their respective amounts (or concentrations) on the surface of the strontium sulphate. Hence, when a strontium sulphate precipitate is shaken up with a saturated solution of strontium sulphate containing a trace of radioactive lead sulphate, an equilibrium is rapidly set up and the following condition holds:

$$\frac{\text{Pb on surf.}}{\text{Pb in soln.}} = K \left(\frac{\text{Sr on surf.}}{\text{Sr in soln.}} \right), \quad (2)$$

where K is a constant. From theoretical considerations, Paneth derived the value of K from the ratio of the strontium and lead concentrations in a solution saturated with respect to both (i.e., K is equal to the ratio of the solubility product constants of the two sulphates).

His results were reproducible and were of the right order of magnitude as compared with the microscope method of determining the surface area. He used the method with Thorium B and Thorium X (a radium isotope) on

barium, strontium, and calcium sulphates. His results were low on the last precipitate, possibly owing to the fact that calcium sulphate is not isomorphous with the others.

Radiostrontium is now available and it was thought that it would be of some interest to check Paneth's indirect method by determining the surface area of a strontium sulphate precipitate by the indirect method using Thorium B and also by the direct method using Sr^{90} , half life 25 years (7).

Experimental

Measurement of Radioactivity

Radioactivity was measured using a thin window Geiger-Müller counter, with an "end on" mica window (3 mgm. per sq. cm.) connected to a scale of 128 scaling circuit (see for example (8)). All activities were corrected for the natural background of the counter, and counter fluctuations were eliminated by comparing the sample with a standard sample of uranium oxide. The statistical counting error was reduced to about 1% by recording 10,000 counts. The resolving time of the counter was determined and corrections made where necessary (9). Additional possibilities of error are those due to pipetting, geometry, back scattering, and self-absorption. The effect of these factors was evaluated empirically. Eight uniform $2\frac{1}{2}$ in. diameter watch glasses were selected and 5 cc. portions of saturated strontium sulphate solution, containing Sr^{90} , pipetted into them. The solution was evaporated under standard conditions on a water bath and the activity counted with the watch glass about 1 in. from the counter window (diameter 1 in.). The ratios with respect to the uranium standard were 1.21, 1.20, 1.24, 1.22, 1.235, 1.255, 1.21, 1.235, showing an average variation from the mean of 1%.

The residue obtained on evaporation of the solution in a typical experiment covers an area of about 15 sq. cm. and weighs about 0.6 mgm. However, the residue deposits in concentric rings and it is therefore not possible to make an accurate calculation of self-absorption. Consequently an empirical test was made. One cubic centimeter of active strontium sulphate solution (containing approximately 0.03 mgm. SrSO_4) was pipetted into each of six watch glasses. Five cubic centimeters of saturated strontium sulphate solution (containing 0.6 mgm. SrSO_4 , the amount used in later experiments) was added to each of three of these, and 5 cc. water added to the other three. The activities after evaporation, agreed to better than 1%, indicating that self-absorption in these experiments is negligible.

Correction for Growth of Daughter, Y^{90}

Sr^{90} decays with emission of a beta particle to Y^{90} which itself decays to Zr^{90} (stable). Y^{90} has a half life of 65 hr. and Sr^{90} , 25 years. Consequently a sample of Sr^{90} , initially free from Y^{90} , will grow Y^{90} quite rapidly. Sr^{90} emits beta particles with energy 0.6 Mev. while Y^{90} emits beta particles with energy 2.2 Mev. The corresponding half-thicknesses for our counter were 25 ± 2 and 205 ± 5 mgm. per sq. cm. of aluminum respectively. The growth

of the Y^{90} daughter may be observed by separating a pure specimen of Sr^{90} and observing its activity from time to time either without a screen between it and the counter or with a screen having a thickness of aluminum of 221 mgm. per sq. cm., between the sample and the counter. In the latter case, all but about 0.2% of the Sr^{90} activity is cut out. The data are recorded in Tables I and II, and plotted in Fig. 1.

TABLE I
GROWTH CURVE OF Y^{90} , WITHOUT SCREENS

Time, hr.	Activity	Correction factor F
0.0	100.0	1.000
0.6	101.0	0.991
2.9	106.2	0.943
4.2	108.2	0.924
5.7	111.0	0.902
10.9	118.6	0.843
22.1	133.5	0.750
51	154.1	0.650
73	171.4	0.585
99	182.4	0.550
119	193.4	0.518
168	202	0.496
192	212	0.472
240	215	0.467
360	225	0.445
576	227	0.441

From Fig. 1 the equilibrium activity due to the Y^{90} is about 130 when the initial Sr^{90} activity is 100. Since Sr^{90} has a much greater half life than Y^{90} the two should be emitting betas at equal rates at equilibrium. The fact that at equilibrium Y^{90} apparently emits 30% more beta particles than the Sr^{90} is due to two causes, (a) there is a much greater absorption of the Sr^{90} beta particles by the air and the window of the counter than for the electrons from Y^{90} , and (b) scattering corrections will differ widely owing to the differing energies of the beta particles (10).

Table II records the data for the growth of Y^{90} as observed through 221 mgm. per sq. cm. of aluminum. Column 2 gives the observed counts per minute, after correcting for the small amount of Sr^{90} betas that passed through the screen. When these figures are plotted against the time, the curve levels out at about 7900 counts per minute. Column 3 is obtained by taking 7900 to be 130%. Fig. 1 indicates that the results of the experiments with and without a screen are in good agreement. Quite obviously, if a sample of Sr^{90} initially free from Y^{90} , is left for a few hours before counting, a correction must be applied to the observed activity in order to find the activity due to Sr^{90} .

Column III of Table I gives the correction factor F for converting the total activity of a sample at a given time to the activity due to the strontium ($F = \text{ratio } 100 : \text{observed activity}$). The values are plotted in Fig. 1 (inset).

TABLE II

GROWTH OF Y^{90} , AS MEASURED THROUGH AN ALUMINUM SCREEN
(221 MGM./SQ. CM. ALUMINUM)

Time, days	Counts/min.	Activity % (normalized)
0.04	135	2.2
0.08	191	3.1
0.25	562	9.2
1.1	2184	35.7
2.1	3713	60.9
3.0	4758	78
4.2	5555	91
6.3	6577	108
7.0	6821	112
8.0	7984	131
10.3	7803	128
21.1	8097	133

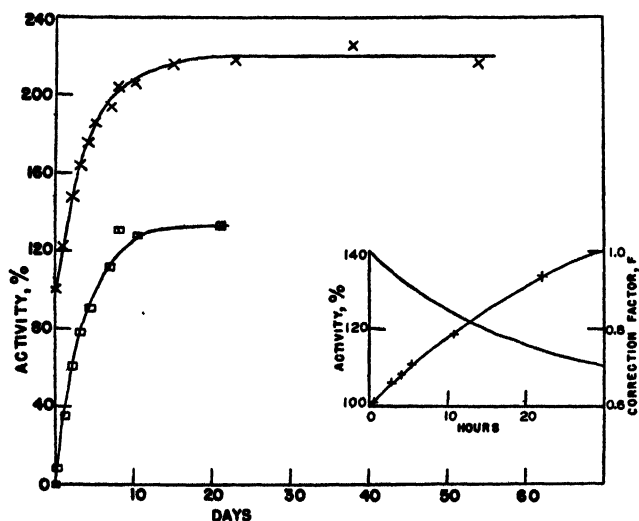


FIG. 1. Growth of Y^{90} daughter. \square , Y^{90} activity; \times , Y^{90} plus Sr^{90} activity.

Preparation of $Sr^{90}SO_4$

Sr^{90} was isolated from a mixture of barium and strontium carbonates that had been separated from fission products more than a year previously. A small sample showed no decay over the course of two months, indicating that Ba^{140} and Sr^{89} were not present in appreciable amounts. As shown below, it eventually became apparent that the activity was due mainly, if not totally, to Sr^{90} and its daughter Y^{90} . Preliminary tests also showed that inactive barium was present in considerable amount but that very little inactive strontium was present. Consequently, 5 mgm. inactive strontium carrier was added to a solution obtained by dissolving these carbonates in acetic acid. Ba^{++} and Sr^{++} were then precipitated as sulphates as a means of separating these from the rare earths, Y^{+++} , La^{+++} , and Ce^{++++} , whose sulphates were soluble under these conditions. After converting the precipitate to carbonates

again and dissolving in acetic acid, barium was removed as chromate. The strontium was precipitated as carbonate and dissolved in acetic acid. The degree of separation was followed by taking absorption curves, using aluminum screens. Fig. 2 shows the progressive change in the absorption curve as the

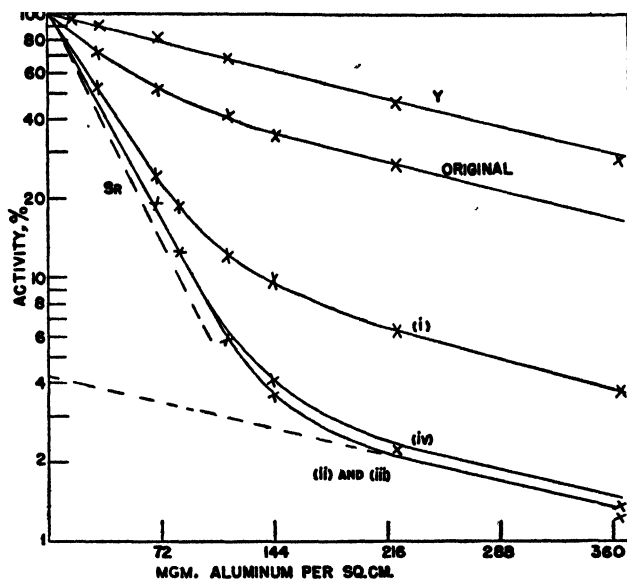


FIG. 2. Change in absorption curve as Sr^{90} is separated from Y^{90} .

strontium is freed from yttrium. Curve (i) is for the material obtained in the first strontium separation described above. Holdback carriers of Y^{+++} , La^{+++} , and Ce^{++++} were then added and the strontium separated as sulphate. The sulphate was converted to carbonate and the sulphate precipitation cycle repeated three times, each time adding rare earth holdback carriers. Curves (ii) and (iii) for the second and third separations were identical and curve (iv) was a little high, owing to the fact that a somewhat longer time elapsed between the separation of the Sr and the measurement of the absorption curve (allowing more Y^{90} to grow) in (iv) than in (ii) and (iii).

The dashed line in Fig. 2 indicates about 4% Y^{90} activity. Since about 3% would have grown in the two hours elapsed between separating and measuring, the separation was at least 99% complete.

The strontium acetate solution from the above four treatments was used in surface area determinations—any Y^{90} that had grown from the Sr^{90} being removed immediately before the surface area experiments.

A sample of Y^{90} was prepared as follows: 0.1 mgm. Y^{+++} and 1 mgm. Sr^{++} were added to a Sr^{90} solution that had been kept for some time. After removing Sr as sulphate, Y^{90} was precipitated as hydroxide with ammonium hydroxide. The resulting precipitate was washed once with ammonium hydroxide solution and dissolved in two drops dilute acetic acid. The solution was diluted to 0.25 cc., 1 mgm. Sr^{++} holdback carrier added, and the separation

repeated. The yttrium hydroxide was dissolved in acetic acid. A small portion of the solution was evaporated and used to determine a decay curve. The results are given in Table III.

TABLE III
DECAY OF Y^{90}

Days	% activity
0	100
6.7	17.37
8.7	10.52
17	1.15

After 63 days there was no measurable activity, indicating the absence of longer lived activities.

A semilog plot of these data indicates that the half life is 65.5 hours.*

Separation of Sr^{90} and Y^{90} Prior to Surface Area Determination

A suitable aliquot of active strontium acetate solution, obtained as above, is placed in a 3 cc. centrifuge tube. One tenth of a milligram of yttrium (as chloride) holdback carrier and 0.5 mgm. of strontium (as nitrate) are added. The volume is made up to about 0.5 cc. and one drop of dilute sulphuric acid is added. The resulting precipitate is digested on a hot water bath for 15 min., centrifuged, and washed twice with cold water. About 0.25 cc. of 10% sodium carbonate solution is added to the strontium sulphate precipitate in the centrifuge tube, and the mixture is heated on the hot water bath for 15 min. with occasional stirring. The precipitate is centrifuged, washed twice with hot water, and dissolved completely in two drops of hot dilute acetic acid. Suitable portions of this active strontium acetate solution were used for specific surface determinations.

Preparation of Strontium Sulphate

Two hundred cubic centimeters of 8 *M* sulphuric acid was added slowly, with stirring, to 500 cc. of 3 *M* strontium chloride solution. During the mixing, which took six minutes, the temperature rose from 22° to 35° C. The suspension was allowed to settle, the clear supernatant solution decanted off, and the precipitate washed six times with 1500 cc. portions of distilled water. The mixture was stirred for 15 min. during each of the first three washings, 30 min. during each of the fourth and fifth washings, and one hour during the last washing. Only a very small amount of the finer particles was lost during this treatment. Finally, the precipitate was transferred to a 1 liter wide mouthed, glass stoppered bottle and diluted to 1 liter with distilled

* It should perhaps be remarked that these results were obtained independently of and prior to the publication of the Manhattan Project report (7).

water. This "suspension B" was used to determine the surface area with Sr^{90} . Roughly 1/10 of suspension B was withdrawn and put into another similar bottle and diluted to 1 liter with saturated strontium sulphate solution. This was labelled "suspension B diluted" and was used to determine the surface area with Thorium B.

The amount of precipitate in 5 cc. of "suspension B" and in 1 cc. of "suspension B diluted" was determined as follows. The suspension was made homogeneous by stirring rapidly with an electrically driven stirrer and, while still stirring, the 5 cc. portion was pipetted off and filtered through a dried and weighed Gooch crucible. The pipette was kept perpendicular while the suspension was in it in order to prevent the precipitate from clinging to the sides. This standard technique of pipetting was used during specific surface determinations. The crucibles were dried in an electric oven at 80°C . to constant weight. Both determinations were run in duplicate. The resulting weights are given below.

WEIGHT OF STRONTIUM SULPHATE IN GRAMS

	1	2	Average
5 cc. of suspension B	1.0716	1.0700	1.0708
1 cc. of suspension B diluted	0.0217	0.0219	0.0218

Preparation of a Saturated Aqueous Solution of SrSO_4

A saturated aqueous solution of strontium sulphate was made up as follows. Ten cubic centimeters of suspension B was put into 5 liters of distilled water and stirred for 24 hr. in a constant temperature bath at $25 \pm 0.05^\circ \text{C}$. The precipitate was then allowed to settle for four hours at the same constant temperature and the clear, supernatant solution was siphoned off and filtered through filter paper into two flasks, A and B.

The amount of solid material in the solution in each bottle was determined by evaporating 1 liter to dryness on a steam bath and weighing the residue. One liter of distilled water was evaporated in a similar manner and the residue weighed. This "blank" was run in duplicate. The results are listed below in grams per liter.

	1	2	Average
Sample	0.1245	0.1252	0.1249
Blank	0.0063	0.0074	0.0069
Solubility			0.1180

From this work, the solubility of strontium sulphate in water at 25°C . was taken to be 0.1180 gm. per liter. This value was used in the specific surface determinations. The Critical Tables do not list the solubility of this salt.

However, a number of values, as determined by various authors, are given in *A Dictionary of Solubilities* by Comey and Hahn. The result obtained here is within the widely fluctuating values listed by these authors. The pH of the solution was 6.75.

Measurement of Adsorption of Sr^{90} by Strontium Sulphate Crystals

Experimental Procedure

The experimental procedure for determining the amount of Sr^{90} adsorbed by a given weight of strontium sulphate was as follows. A portion of Sr^{90} was separated from Y^{90} using the standard procedure given on p. 244. The time at which the strontium sulphate (active) was precipitated during this separation was recorded. A small portion of the resulting strontium acetate solution was added to a given volume of the saturated strontium sulphate solution. Its concentration was such that the strontium concentration of this "solution A" was not increased appreciably but its resulting activity was sufficiently large to give accurate counting values during subsequent specific surface determinations.

Five cubic centimeters of suspension B was pipetted into a 30 cc. glass stoppered bottle made of flint glass. Fifteen cubic centimeters of solution A was then pipetted into this bottle and the latter was shaken for a given length of time. (The temperature of the suspension was kept at 25° C. while shaking.) It will be shown later that varying the method of shaking makes no appreciable difference to the amount of activity adsorbed. The suspension was then centrifuged for about three minutes, 5 cc. of the supernatant liquid pipetted off and evaporated on a watch glass on a hot water bath, and its activity determined on the counter. The activity of the original was determined by evaporation of two 5 cc. portions of solution A on similar watch glasses and counting. The average of these multiplied by 0.76 was used as a standard instead of the normal uranium oxide standard.* All results were obtained in duplicate. The times of centrifuging and counting were noted. All sample readings were sandwiched between the readings of the original solution A. From the ratio of the sample to the original, after each was corrected for the growth of the yttrium daughter, the percentage of Sr^{90} adsorbed could be obtained.

These experiments were carried out with suspension B after it had stood in the laboratory for 60 days.

Method of Calculation

It is shown later that yttrium ions are not adsorbed appreciably on the surface of a strontium sulphate precipitate that is in contact with a saturated solution of strontium sulphate containing yttrium.

* This factor depends on the volume of the precipitate. Taking the density of strontium sulphate as 4, the volume of the precipitate in 5 cc. of suspension B is roughly, 0.27 cc. Thus the final volume of the solution is 19.73 (not 20 cc.) and the factor is $\frac{15}{19.73} = 0.76$.

Having established the above fact, the percentage Sr^{90} adsorbed may be calculated from the ratio of the activities of the supernatant liquid and the original solution.

Let the time between the separating of the Sr^{90} and the centrifuging be t_1 and let the time between the centrifuging and the counting be t_2 . Let the correction factors taken from Fig. 1 for these times be F_1 and F_2 and let the factor for the time $t_3 = t_1 + t_2$ be F_3 . Let the ratio of the measured activities of the supernatant liquid and the original be R . Then, assuming the original activity to be 100 units at time t_3 , the sample activity is $100R$ units. The Sr^{90} in the original = the total Sr^{90} in the sample before centrifuging = $100 \times F_3$.

The total activity at the time of centrifuging = $\frac{100 \times F_3}{F_1}$. Therefore the Y^{90} activity that built up in the sample before centrifuging

$$= \frac{100 \times F_3}{F_1} - 100 \times F_3.$$

It is shown later that this Y^{90} stayed in the solution when the sample was centrifuged. During the subsequent " t_2 " hours before counting, some of this Y^{90} decayed and, using the half life of 65.5 hr., a correction factor k may be found so that, at the time of counting, this excess Y^{90} had dropped to

$$k \left[\frac{100 \times F_3}{F_1} - 100 \times F_3 \right]$$

Let X = the units of Sr^{90} not adsorbed on the surface of the precipitate. Then, the Y^{90} that grew from X in t_2 hours = $\frac{X}{F_2} - X$.

At time t_3 , the total activity in the sample of supernatant liquid = the activity of unadsorbed Sr^{90} + the activity of Y^{90} that built up before centrifuging + the activity of Y^{90} that built up after centrifuging, or

$$\begin{aligned} 100R &= X + k \left[\frac{100 \times F_3}{F_1} - 100 \times F_3 \right] + \frac{X}{F_2} - X \\ &= k \left[\frac{100 \times F_3}{F_1} - 100 \times F_3 \right] + \frac{X}{F_2}. \end{aligned}$$

Rearranging,

$$X = F_2 \left\{ 100R - k \left[\frac{100 \times F_3}{F_1} - 100 \times F_3 \right] \right\}.$$

The Sr^{90} adsorbed on the precipitate

$$= 100 \times F_3 - X = F_3 \left\{ 100 - F_2 \left[\frac{100R}{F_3} - k \left(\frac{100}{F_1} - 100 \right) \right] \right\}.$$

The % Sr^{90} ads. = $\frac{\text{units of } \text{Sr}^{90} \text{ ads.}}{\text{units of } \text{Sr}^{90} \text{ in original}} \times 100$

$$= 100 - F_2 \left[\frac{100R}{F_3} - k \left(\frac{100}{F_1} - 100 \right) \right].$$

An example of the use of this equation is as follows:

- (i) Activity of original = 4040 counts per minute (at 3.30 p.m.),
- (ii) Activity of supernatant liquid = 982 counts per minute (at 3.30 p.m.),
- (iii) Time of separation of Sr^{90} = 9.00 a.m.
- (iv) Time of centrifuging = 11.45 a.m.

The corrected original (see p. 246) = $4040 \times 0.76 = 3070$. Then $R = \frac{982}{3070} = 0.320$. $t_1 = 2.75$ hr., $t_2 = 3.75$ hr. and $t_3 = 6.50$ hr. From Fig. 1, the correction factors are: $F_1 = 0.95$, $F_2 = 0.93$, and $F_3 = 0.89$.

At time $t_2 = 3.75$ hr., $k = 0.96$ (approx.)

Substituting in the above equation:

$$\begin{aligned} \% \text{ Sr}^{90} \text{ ads.} &= 100 - 0.93 \left[\frac{100 \times 0.32}{0.89} - 0.96 \left(\frac{100}{0.95} - 100 \right) \right] \\ &= 71.1. \end{aligned}$$

All "% Sr ads." values were calculated in this manner.

Effect of Time of Shaking

In order to determine the effect of time of shaking, experiments were carried out in which the time of shaking was varied. The general procedure outlined above was followed using 5 cc. of suspension B which contained 1.0708 gm. of SrSO_4 . The results are given in Table IV. Each experiment was done in duplicate.

TABLE IV

(SEE FIG. 3)

EFFECT OF TIME OF SHAKING

Min. shaken	Method of shaking	%Sr ⁹⁰ ads.		
		Experiment 1	Experiment 2	Average
0.1	By hand	40.0	38.2	39.1
1	"	48.5	45.9	47.2
5	"	47.9	47.1	47.5
10	"	50.1	48.7	49.4
10	Automatic	50.7	49.5	50.1
15	By hand	51.8	49.8	50.8
30	"	56.2	55.2	55.7
60	"	59.0	57.6	58.3
120	Automatic	61.2	59.6	60.4
240	"	59.3	58.9	59.1

It should be mentioned here that the delay in transferring the suspension from the shaking bottle to the centrifuge tube, during which time the precipitate was still in contact with the solution, was in no case greater than two minutes and, for the shaking times of 0.1 and 1 minute, it was about 1 minute.

The two sets of results in Table IV, one obtained by shaking for 10 min. by hand, and the other by shaking for 10 min. with the automatic shaker (Gyrosolve), agree within 0.7%. This indicates that no serious difference is introduced by using different shaking methods.

The results are plotted in Fig. 3 as "% Sr⁹⁰ adsorbed" versus time of shaking in minutes. From the rapid initial rise in this time curve (from zero

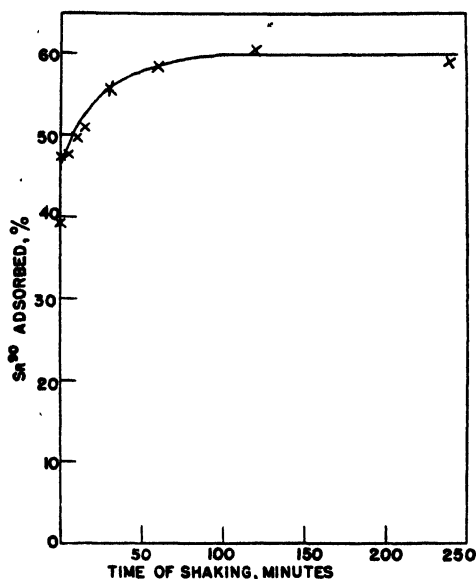


FIG. 3. Effect of time of shaking on percentage adsorption of Sr⁹⁰.

to about 47% of Sr⁹⁰ adsorbed in one minute) it appears that the primary exchange reaction is complete in less than one minute. The further slow rise is probably due to a slow secondary process or processes.

The curves obtained by Paneth and Vorwerk (6) and by Kolthoff and Rosenblum (2, p. 2659; Table III, preparation II) using nondried lead sulphate precipitates and Thorium B are quite similar to this curve. However, Paneth followed his for about 30 min. only. Kolthoff followed his for 24 hr. and found that it kept rising slowly.

The specific surface was calculated from the average percentage Sr⁹⁰ adsorbed after 10 min. of shaking (49.8%). While there is a certain arbitrariness about the time chosen, it appears likely that less than 3% of the 49.8% was due to slow secondary processes since 46.9% was adsorbed in one minute, during which time the effect of these slow reactions was probably negligible.

The Calculation of the Surface Area of SrSO₄ Using Sr⁹⁰ (Direct Method)

The specific surface of the precipitate in suspension B may be calculated as follows:

$$\text{Gm. Sr in surface per gm. SrSO}_4 = \frac{\% \text{Sr}^{90} \text{ ads.}}{100 - \% \text{Sr}^{90} \text{ ads.}} \times \frac{\text{gm. of Sr in soln.}}{a}, \quad (3)$$

where a is the weight of the strontium sulphate precipitate. The "%Sr⁹⁰ ads." after 10 min. of shaking is 49.8 (see Table IV). For suspension B, a is equal to 1.0708 gm. (see p. 245). The weight of strontium sulphate in 1 liter of saturated solution was found to be 0.1180 gm. (see p. 245). Therefore, the "gm. of Sr in soln." is equal to

$$\frac{19.73}{1000} \times 0.1180 \times \frac{87.63}{183.69} = 11.1 \times 10^{-4}$$

Substituting these values into Equation (3);

$$\begin{aligned} \text{Gm. Sr in surface per gm. SrSO}_4 &= \frac{49.8}{100 - 49.8} \times \frac{11.1 \times 10^{-4}}{1.0708} \\ &= 10.3 \times 10^{-4} \end{aligned}$$

The number of atoms of strontium or molecules of strontium sulphate on the surface of 1 gm. = $\frac{10.3 \times 10^{-4}}{87.63} \times 6.02 \times 10^{23} = 7.06 \times 10^{18}$.

The volume occupied by one "molecule"* of strontium sulphate

$$= \frac{183.69}{\text{Sp. gr.} \times \text{Av. No.}} = \frac{183.69}{3.96 \times 6.02 \times 10^{23}} = 77 \times 10^{-24} \text{ cc.}$$

Then, the area represented by one side of a molecule, assuming a cubic lattice = $(77 \times 10^{-24})^{2/3} = 18.1 \times 10^{-16}$ sq. cm. Therefore, the surface area of 1 gm. of precipitate = $7.06 \times 10^{18} \times 18.1 \times 10^{-16} = 12,800$ sq. cm.

The 2% error in determining "% Sr⁹⁰ ads." results in a 4% error in the specific surface or the surface area. The error in the determination of a is less than 1% and the discrepancy in "gm. of Sr in soln." is probably less than 1%. Therefore, the surface area of 1 gm. of the precipitate is equal to 12,800 sq. cm. ($\pm 5\%$).

Aging of the Precipitate

In order to ascertain the effect of aging on the size of the crystals, the specific surface of suspension B was redetermined after it had stood in the laboratory for a few months. The procedure already described was used with a shaking time of 10 min. The "gm. of Sr. in soln." of Equation (3) was taken to be the same as before. The results are given below together with those that were previously obtained.

Age, days	Gm. of strontium sulphate in 5 cc. of suspension B	% Sr ⁹⁰ ads.	Sp. surf.
70	1.071	49.8	12,800 sq. cm. per gm.
225	1.060	49.4	12,700 sq. cm. per gm.

* The "molecule" is one strontium ion plus one sulphate ion.

These results show that the surface area did not change during the period from 70 to 225 days after the formation of the precipitate. This fact is of importance because the specific surface was determined with Thorium B during this period.

Adsorption of Y^{+++} on Strontium Sulphate Crystals

A portion of the active yttrium acetate was added to an aqueous, saturated solution of strontium sulphate. Five cubic centimeters of suspension B was made up to 20 cc., with this active solution, in a shaking bottle. Twenty cubic centimeters of the active solution was added to another bottle as a blank. Both bottles were shaken for four hours. The suspension was centrifuged and 5 cc. portions of the supernatant solution and of the blank were evaporated in watch glasses on a hot water bath. The experiment was done in triplicate. The blank was multiplied by a correction factor of 0.76 as on page 246. The ratio of all of the readings to the third blank are given in the table below. The percentage Y^{90} adsorbed, as obtained from this ratio, is given in the third column.

	Ratio	% Y^{90} ads.
Blank — (1)	1.015	
Blank — (2)	1.980	
Blank — (3)	1.000	
Sample — (1)	1.056	-5.6
Sample — (2)	1.046	-4.6
Sample — (3)	1.023	-2.3

The average % Y^{90} adsorbed = -4.2%. The negative result indicates that yttrium is not adsorbed on the surface of a strontium sulphate precipitate that is in contact with an aqueous, saturated solution of strontium sulphate containing Y^{90} .

Adsorption of Sr^{90} on Flint Glass

In order to determine whether Sr^{90} was being adsorbed on the walls of the flint glass bottles during the shaking period, 20 cc. of the active saturated solution of strontium sulphate was shaken for four hours on the automatic shaker in one of the flint glass bottles, and 5 cc. of this solution was then evaporated on a 2½ in. watch glass and counted. This experiment was carried out in duplicate. Five blanks were made by evaporating 5 cc. portions of the same active solution, on similar watch glasses, and counting. These blanks were withdrawn from the active stock solution and evaporated at various times before and during the shaking of the duplicate solutions so as to determine whether or not any adsorption of Sr^{90} occurred on the walls of the stock bottle while standing. The activities of the samples, after shaking, were compared with the blanks. The growth of the yttrium daughter was the same for the samples and the blanks, and could therefore be neglected. The ratios of the

blanks to the average blank and the ratios of the sample activities to the average blank are listed below. The second column gives the apparent Sr^{90} activity adsorbed when the solutions were shaken for four hours. Blank 4 was used as the standard.

	Ratio	% Adsorbed
Blank 1	1.04	
Blank 2	0.99	
Blank 3	0.97	
Blank 4	1.00	
Blank 5	1.00	
Sample 1	0.98	2
Sample 2	0.99	1

The fact that the ratios of the blanks are close together indicates that no adsorption of activity took place on the walls of the stock bottle during the four hours' shaking time. The average percentage adsorbed (1.5%) is within the limit of experimental error. Thus, it was concluded that Sr^{90} is not adsorbed appreciably on the walls of the flint glass shaking bottle during the four hours' shaking.

Summing up the possible effect of the various errors, it is thought that they would not be greater than 5%. Kolthoff and Rosenblum (2) allowed an error of 2% for their determination of the adsorption of ThB on lead sulphate.

The Calculation of the Surface Area of Strontium Sulphate Using Thorium B (Indirect Method)

Experiments were done using ThB that had been separated from Thorium nitrate (a) chemically and (b) by the emanation method.

(a) Chemical Separation

To 12 gm. thorium nitrate was added 12 cc. water, 2 mgm. Pb^{++} carrier and 1 mgm. of each of Ba^{++} and La^{+++} (nitrates) as holdback carriers for radium and actinium. Lead sulphide was precipitated by passing hydrogen sulphide through the hot solution. The precipitate was digested, centrifuged, washed, and dissolved in hot nitric acid. The free sulphur was centrifuged off and the solution evaporated to dryness. The white solid was taken up in a small amount of water. A small portion of this solution was evaporated on a slide which was used to determine the half life of ThB. The value found (10.6 hr., Fig. 4) agrees with the accepted. The remainder of the solution was added to 45 cc. saturated strontium sulphate solution (solution C).

Thorium B (Separated Chemically) Adsorbed by SrSO_4

One cubic centimeter portions of "suspension B diluted" were pipetted into each of three 30 cc. glass stoppered shaking bottles. Ten cubic centimeter portions of solution C were pipetted into each bottle and the bottles were

shaken on the shaker for 10 min. The samples were quickly centrifuged and 5 cc. of each clear filtrate was evaporated on the steam bath in the same type of watch glass as used in determining the specific surface with Sr^{90} . Three

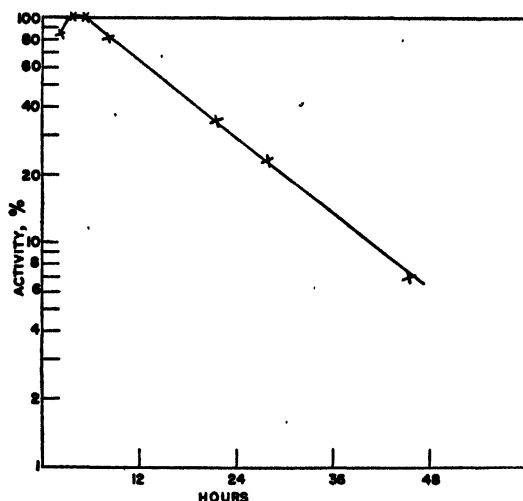


FIG. 4. Decay curve for ThB; half life 10.6 hr.

5 cc. portions of solution C were evaporated in similar watch glasses to serve as blanks. Counts were taken eight hours after centrifuging in order to allow the residues to reach radioactive equilibrium (see Fig. 4). The average activity of the three blanks was determined. The ratio of the three samples to this average blank was obtained. Then, allowing for the dilution factor,

% ThB ads. = $100 \left(1 - \text{ratio} \times \frac{11}{10} \right) \cdot *$ The results are given below.

	%ThB ads.
1	57.5
2	55.3
3	57.4

The average value is 56.7%.

The Surface Area

The specific surface may be calculated by inserting Paneth's theoretical K value into Equation (3).

$$\text{Gm. Sr in surface per gm. SrSO}_4 = \frac{1}{K} \times \frac{\% \text{ThB ads.}}{100 - \% \text{ThB ads.}} \times \frac{\text{gm. of Sr in soln.}}{a}$$

$$K = 15$$

$$\% \text{ThB ads.} = 56.7$$

$$\begin{aligned} \text{Gm. of Sr in 11 cc. of soln.} &= \frac{87.6}{183.7} \times 0.118 \times \frac{11}{1000} \\ &= 6.19 \times 10^{-4}. \end{aligned}$$

* The volume of crystalline strontium sulphate will not alter the factor 11/10 appreciably.

Substituting these values into the above equation,

$$\begin{aligned}\text{Gm. Sr in surface per gm. SrSO}_4 &= \frac{1}{15} \times \frac{56.7}{100 - 56.7} \times \frac{6.19 \times 10^{-4}}{0.0218} \\ &= 24.8 \times 10^{-4}.\end{aligned}$$

The number of molecules of strontium sulphate on the surface of 1 gm. of precipitate = $\frac{24.8 \times 10^{-4}}{87.63} \times 6.02 \times 10^{23} = 17.04 \times 10^{18}$.

It has been previously shown (page 250) that the surface area covered by one molecule of strontium sulphate = 18.1×10^{-16} sq. cm. Therefore the surface area of 1 gm. of precipitate = $17.04 \times 10^{18} \times 18.1 \times 10^{-16} = 30,800$ sq. cm.

The counting, geometrical, and mechanical errors were such that the specific surface obtained here is precise to within $\pm 5\%$.

Since the Thorium B was allowed to reach radioactive equilibrium before counting, the adsorption of Thorium C (bismuth) on the precipitate, if it occurred at all, did not affect the final activity that was measured. For the same reason, any self-absorption of the beta particles from ThB and its daughters would occur to the same extent in the blanks and the samples.

It was found by direct experiments similar to those with Sr^{90} that Thorium B was not adsorbed on the walls of the flint glass shaking bottle after 10 min. of shaking when less than 1 mgm. of lead carrier per 20 cc. of saturated strontium sulphate was used in the presence of small amounts (of the order of $10^{-3} N$) of nitric or of acetic acid.

Mention should be made of some earlier, somewhat less accurate experiments. Using 0.07 gm. strontium sulphate and half as much lead carrier as in the above experiments, a specific surface of 24,000 sq. cm. was obtained, while using five times as much lead carrier a specific surface of 24,400 sq. cm. was obtained. This indicates that a 10-fold variation in the ratio of lead carrier to strontium sulphate precipitate does not affect the calculated surface area appreciably. Experiments on the effect of time of shaking gave results very similar to those for Sr^{90} .

(b) *Emanation method*

Preliminary experiments indicated that thorium nitrate crystals gave off very little emanation. However, when the nitrate was converted to hydroxide a high Thorium B activity was obtained by the emanation method. Two hundred and fifty grams thorium nitrate was converted to the hydroxide, which was dried at room temperature and powdered and placed in a flat bottomed dish, 10 in. in diameter. The dish was placed in a tin can and a platinum foil was suspended in the center of the can by a wire passing through an insulating stopper. The foil was made 75 v. negative with respect to the can. An activity of 40,000 counts per minute collected on the foil in two days. After reaching equilibrium it decayed with a half life of 11 hr. ($\pm 5\%$) and was evidently Thorium B.

Surface Area Measurement Using ThB (Emanation)

Preliminary experiments indicated that Thorium B, obtained by the emanation method, was adsorbed quite strongly on glass. This was in agreement with the findings of Kolthoff and Eggertson (1). In order to eliminate this difficulty the glassware was coated with paraffin wax. The pipettes were then standardized. As a further precaution, a very small amount (10^{-6} gm.) of lead carrier was used. In this way, adsorption on the walls of the vessels during a specific surface determination was reduced to about 5%.

The procedure used in the final surface area determination of suspension B was as follows. One cubic centimeter of "Suspension B diluted" was pipetted into a paraffin coated shaking bottle. (Paraffin coated equipment was used in each of the following steps.) The platinum foil from the emanation apparatus was stirred by hand for 10 min. in 40 cc. of saturated strontium sulphate solution to which 10^{-6} gm. of lead carrier (as lead nitrate) had been added. This procedure removed approximately one-half of the activity from the foil. The resulting active solution was centrifuged for 10 min. and a certain portion of this "solution D" was pipetted into the shaking bottle containing the "suspension B diluted". The bottle was shaken by hand for 10 min. The solution was centrifuged for one minute and an aliquot was pipetted into a watch glass. A similar aliquot of solution D was pipetted into a similar watch glass to serve as a blank. The solutions were then evaporated on a hot water bath, allowed to stand for eight hours in order to reach radioactive equilibrium, and their relative activities determined in the usual manner with a Geiger counter. Both samples and blanks were run in duplicate. The dilution of the samples with 1 cc. of "Suspension B diluted" as well as the small adsorption of Thorium B on the vessel walls was allowed for in the calculation.

Results

The results obtained in the above experiment are as follows:

	% ThB ads.
Experiment 1	45.1
Experiment 2	46.9
Average	46.0

The average percentage Thorium B adsorbed is 46.0. The volume of saturated strontium sulphate solution was 11.76 cc. The weight of strontium sulphate in 1 liter of saturated solution = 0.1180 gm. (see page 245). Therefore, "gm. of Sr in soln." = $\frac{11.76}{1000} \times 0.1180 \times \frac{87.63}{183.69} = 6.62 \times 10^{-4}$.

$$a = 0.0218 \text{ (see page 245).}$$

$$\begin{aligned} \text{Thus, gm. Sr in surface per gm. SrSO}_4 &= \frac{1}{15} \times \frac{46}{54} \times \frac{6.62 \times 10^{-4}}{0.0218} \\ &= 17.2 \times 10^{-4}. \end{aligned}$$

Using a calculation similar to that used on page 250, the surface area may be calculated to be equal to 21,300 sq. cm. per gram.

Summary of Experimental Results and Conclusion

To summarize, the following results were obtained for the specific surface of a strontium sulphate precipitate:

- | | |
|---|------------------------|
| 1. Direct method (Sr^{90}) | 12,800 sq. cm. per gm. |
| 2. Indirect method (ThB by chemical separation) | 30,800 sq. cm. per gm. |
| 3. Indirect method (ThB by emanation) | 21,300 sq. cm. per gm. |

The third value (21,300 sq. cm.) was obtained by following Paneth and Thimann's indirect method (5) as closely as possible. Comparing this with the value by the direct method (12,800 sq. cm.), it is seen that the direct and indirect methods yield specific surface areas of the same order of magnitude but differing by about 65%. Since this is quite outside the limits of experimental error it would seem that the discrepancy is due to the uncertainty in K .

A simple calculation using Equation (3) and the above values indicates that in order to get better agreement between the direct and indirect methods, K would have to be about 25. It is unfortunate that the $K_{s,p}$'s for lead sulphate and strontium sulphate are not more accurately known. However in spite of the lack of exact agreement between the direct and indirect methods, it is very striking that in order to get 50% "adsorption" of Pb^{212} one needs only $1/25$ the amount of strontium sulphate crystals necessary to give 50% "adsorption" * of Sr^{90} . The Langmuir type of explanation for this would be to say that lead is more strongly adsorbed on the surface than strontium or that it stays on the surface longer, i.e. the "accommodation coefficient" is greater. That the forces are stronger is shown by the smaller solubility of lead sulphate as compared to strontium sulphate and, as mentioned above, Paneth tried to allow for this by putting in the factor K , equal to the ratio of the $K_{s,p}$'s. The situation is complicated by the fact that the Pb is being adsorbed on SrSO_4 and not on PbSO_4 and perhaps a better approach would be to use the indirect tracer method to study surface forces (4), particularly since radioisotopes of most of the elements are now available.

This difference in surface areas by the indirect method, for the two methods of preparing Pb^{212} , calls for comment. Had the removal of Pb^{212} been a case of pure adsorption (unaccompanied by exchange), the minute amount of lead present in the emanation method should have been adsorbed to a greater percentage than in the experiment where Pb^{212} was separated in the presence of a large amount of carrier (larger by a factor of about 10^8). Actually the reverse was true, 57% as compared to 46%, which would seem to rule out the simple adsorption idea and favor the exchange mechanism. The difference in surface areas might well be due to the measured surface area being a function of the nature of the surface as well as the actual area, the nature of the surface

* In view of the loose usage of "adsorption" it might be better to introduce the term "exchange adsorption" to cover this particular type of adsorption.

depending on the extent to which it is covered by exchanging ions. This might be investigated by systematically varying the carrier concentration in the indirect method.

Acknowledgment

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EXCHANGE REACTIONS OF Co^{++} , Co^{+++} , AND THEIR HEXAMMINO COMPLEXES¹

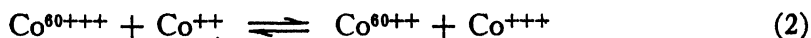
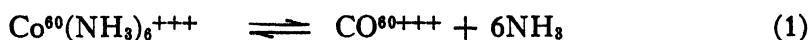
By S. A. HOSHOWSKY², O. G. HOLMES, AND K. J. MCCALLUM

Abstract

In a study of the exchange of radioactive cobalt between Co^{++} and $\text{Co}(\text{NH}_3)_6^{+++}$ it was found that no exchange within experimental error occurred within seven days at 25° C., or two days at 50° C. The various steps involved in a conceivable mechanism by which exchange might have been expected to occur were then investigated separately. From the results obtained it appears that dissociation of the complex is one limiting factor. The exchange between the two hexammino complexes of divalent and trivalent cobalt was found to be very slow at 25° C.

Introduction

In acid or neutral solution, a possible mechanism for exchange of the radioactive cobalt isotope of mass 60 between cobaltous ion and radioactive hexammino cobaltic ion is the following:



If the first equilibrium is operative, as suggested by Lamb and Larson (3) who give the value 2.2×10^{-34} for the instability constant of the complex, a small concentration of cobaltic ion will be present in the solution. An exchange by electron transfer between the uncomplexed cobaltous and cobaltic ions would then result in an eventual exchange of the radioactive cobalt initially present in the solution.

Experiments previously reported (2, 4) have shown that no exchange within experimental error occurs in a period of 24 hr. at room temperature. In explanation of this fact, Flagg (2) suggested that the rate of reduction of the cobaltic ion by water might be greater than the rate of the electron transfer process. However, the reduction of the cobaltic ion would result in the gradual decomposition of the hexammino cobaltic ion, and in view of the observation (4) that less than 0.1% of the complex was so decomposed in 24 hr., either the dissociation of the complex, the reduction of the cobaltic ion, or both, must be considered slow processes.

In the present work, the exchange between the cobaltous and hexammino cobaltic ions has been studied for periods of time up to one week and at both 25° C. and 50° C. The exchange between uncomplexed cobaltic ion and radioactive hexammino cobaltic ion, suggested by Reaction (1), and the electron transfer between the uncomplexed cobaltous and cobaltic ions have been investigated.

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In addition, exchange between the hexammino cobaltous and hexammino cobaltic ions has been studied at room temperature for periods up to 17 days.

Materials

For this study, use was made of the radioactive cobalt isotope of mass 60 with a 5.3 year half life. Radioactive hexammino cobaltic chloride was synthesized by a standard procedure (1). The material was purified by recrystallization, and analyzed for cobalt. The results of duplicate determinations showed 22.08% Co (theoretical: 22.03% Co).

Cobaltic sulphate was prepared by electrolytic oxidation of cobaltous sulphate in sulphuric acid (5). The product was analyzed for total cobalt by electrolytic deposition on weighed copper disks, and for trivalent cobalt by the addition of excess potassium iodide followed by titration with sodium thiosulphate. Although the prepared material was kept at 0° C., the amount of divalent cobalt present in the sample slowly increased owing to the decomposition of the cobaltic ion.

Procedure and Results

I. *Investigation of Exchange between Co^{++} and $\text{Co}(\text{NH}_3)_6^{+++}$*

In these experiments, known amounts of the complex chloride and cobaltous chloride were dissolved in water and the solutions allowed to stand in the dark for known periods of time. Solid ammonium chloride and ammonium thiocyanate were then added, and the cobaltous thiocyanate complex was extracted with ether – isoamyl alcohol mixture. The cobalt was removed from the organic layer by shaking with a dilute ammonia solution and then precipitated by the addition of ammonium sulphide. The cobalt sulphide was dissolved in aqua regia and the resulting solution boiled with sulphuric acid. The cobalt was deposited electrolytically on weighed copper disks and the radioactivity determined. Radioactivity measurements were made using a mica window end-on type of counter with a scale-of-64 circuit. In all cases, corrections for self-absorption were negligible owing to the thin samples used.

In most of the experiments, the radioactivity was initially present in the hexammino cobaltic chloride. In a few experiments, where the radioactivity was initially present in the divalent state, the complex remaining in the aqueous layer, after the extraction with ether – isoamyl alcohol mixture, was precipitated as a double salt by the addition of mercuric chloride. Separation of the cobalt and mercury was carried out by standard procedures, and the cobalt subsequently deposited electrolytically for counting.

In those experiments where the activity was initially present in the complex ion, blank experiments (without the addition of cobaltous chloride) were performed to determine if decomposition of the cobaltic complex to cobaltous ion was occurring under the conditions of these experiments. In these cases, a small amount of cobaltous chloride was added as carrier immediately after the extraction to assist in the electrical deposition.

The results are summarized in Table I, where the mean of duplicate experiments is recorded for each set of conditions. The total number of counts taken for each of the different experiments varied between 2400 and 6000

TABLE I
EXCHANGE BETWEEN $\text{Co}(\text{NH}_3)_6^{+++}$ AND Co^{++}
Solutions 0.011 molar in both forms of cobalt

Temperature, °C.	Time	Apparent per cent exchange
25	3.5 hours	$0.03 \pm 0.05^*$
25	3.5 hours	0.02 ± 0.07
25	6 hours	$0.06 \pm 0.07^{**}$
25	6 hours	$0.01 \pm 0.06^{**}$
25	1 day	0.03 ± 0.07
25	7 days	-0.10 ± 0.11
50	1 day	-0.10 ± 0.15
50	2 days	-0.15 ± 0.18
50	3 days	0.70 ± 0.28
50	6 days	$+0.90 \pm 0.13$

* Solution 1 molar in hydrochloric acid.

** Radiocativity initially present in the divalent state.

counts per minute. The results are reported as the apparent percentage of the hexammino cobaltic chloride undergoing exchange with all of the divalent cobalt present. The uncertainties were calculated, taking the statistical error in the determination of the background and cobalt activity as the square root of the number of counts observed.

At 25° C., exchange is found to be zero within experimental error for periods up to seven days. At 50° C., a small but measurable exchange is found to occur within six days. In the latter case, a correction has been made for the decomposition of 0.4% of the complex to form cobaltous ions, which was detected in the blank experiments.

II. Investigation of the Exchange between Co^{+++} and $\text{Co}(\text{NH}_3)_6^{+++}$

A study of the exchange between hexammino cobaltic ion and the uncomplexed cobaltic ion was made to give information on the equilibrium represented by Reaction (1). If this equilibrium is rapidly and completely established, an exchange between radioactive hexammino cobaltic ions and cobaltic ions should be observable.

Cobaltic sulphate was used as the source of cobaltic ions. In solution it is quite likely that the cobaltic ions are hydrated so that the exchange being investigated is one between the hexammino complex and an aquo complex. The known behavior of the cobaltic ion in aqueous solution indicates that the stability of such a complex must be small.

The ease of reduction of the cobaltic ion to the divalent state by water is a complicating factor in the study of this exchange reaction. At low temperatures, the reduction is slow enough to permit experiments to be carried out.

The general procedure was as follows. To a 0.01 molar solution of radioactive hexamino cobaltic sulphate was added cobaltic sulphate so that the two forms of trivalent cobalt were in equimolar proportions. Owing to the reaction of the cobaltic ion with water, the concentration of this ion gradually decreased. The solution was allowed to stand until one-third of the cobaltic ion initially added remained in the trivalent state, a period of time determined in a separate experiment. The remainder of the cobaltic ion was then reduced to the cobaltous state and the uncomplexed cobalt separated from the hexamino cobaltic complex by extraction with ammonium thiocyanate and amyl alcohol - ether mixture.

Exchange during the process would result in the appearance of radioactivity in the form of cobaltic ions, which were subsequently reduced to the cobaltous state. Detection of radioactivity in the extracted cobaltous fraction would then indicate the occurrence of an exchange.

Similar experiments were carried out using the perchlorate anion in place of the sulphate ion. The hexamino cobaltic chloride and cobaltic sulphate were converted into the corresponding perchlorate salts by the addition of the calculated amounts of silver perchlorate and barium perchlorate, respectively.

The mean results of duplicate experiments are given in Table II. The results indicate that under the conditions of these experiments, exchange is zero within experimental error.

TABLE II
EXPERIMENTS ON $\text{Co}^{+++} - \text{Co}(\text{NH}_3)_6^{+++}$ EXCHANGE
Solutions 0.01 molar in cobalt

Solution	Temperature, °C.	Time, hr.	Average per cent activity in uncomplexed cobalt
0.5 M H_2SO_4	0	5	0.08 ± 0.11
0.01 M H_2SO_4	0	1.5	0.18 ± 0.18
0.5 M H_2SO_4	20	1.5	0.09 ± 0.12
0.02 N HClO_4	0	4	0.02 ± 0.19
0.02 N HClO_4	20	0.5	0.01 ± 0.18

III. Investigation of Electron Transfer between Co^{++} and Co^{+++}

The exchange of radioactive cobalt between these two valence states can, in principle, occur by an electron transfer process. Studies on this process are complicated by the instability of the cobaltic ion in solution. Furthermore, the separation of the cobaltous and cobaltic ions is not simple, the solvent extraction method not being applicable because of the rapid reduction of the cobaltic ion which occurs during the attempted separation.

The general procedure in the investigation was to dissolve an equimolar quantity of cobaltic sulphate in a 0.01 molar solution of radioactive cobaltous sulphate at 0° C. Of several separation procedures attempted, the following were the most satisfactory.

When potassium nitrite is added to a solution of a cobaltous salt in the presence of dilute acid, there is readily formed a precipitate of potassium cobaltinitrite, the cobaltous ions having been oxidized to the trivalent state. However, a neutral solution does not form a precipitate within 10 min. at 0° C. A neutral solution containing cobaltic ions, on the other hand, forms a precipitate within one minute under the same conditions. No oxidation need occur in this latter case. This method was applied in the separation process, using freshly precipitated zinc hydroxide as the neutralizing agent.

After the precipitate in neutral solution had been obtained, it was removed by centrifugation, and the remainder of the cobalt precipitated by the addition of dilute acetic acid. The cobalt from both precipitates was deposited on weighed copper disks and the activity determined.

The results of duplicate experiments showed that, four minutes after mixing the two forms of cobalt, the specific activities of both fractions were within 5% of that expected if complete exchange had occurred. Thus, within the time required to achieve separation of the cobaltous and cobaltic ions by this precipitation method, exchange was complete within experimental error.

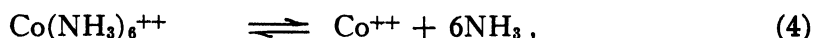
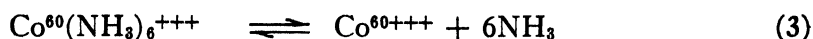
A second method of separation was by chromatographic adsorption. Ignited aluminum oxide was found to make a satisfactory adsorption column for the separation of cobaltous and cobaltic ions. The blue cobaltic ions remained adsorbed near the top of the column while the pink cobaltous ions were adsorbed near the bottom and could be washed through into the filter flask. Owing to the decomposition of the cobaltic ions by water, the separation had to be achieved as rapidly as possible. Several types of column were tried, but the following proved most satisfactory.

The column was prepared by pouring a slurry of alumina powder on a Büchner funnel placed in a filter flask. The thickness of the alumina layer varied between $\frac{1}{2}$ and 1 cm. The adsorbent was packed and washed with water at 0° C., and then the solution containing cobaltic sulphate and radioactive cobaltous sulphate, both at 0.01 molar concentration, was poured through the column. The cobaltous sulphate was eluted by washing immediately with 75 ml. of 1 molar sulphuric acid which had been cooled to 0° C. The alumina containing the adsorbed cobaltic ions was then stirred rapidly into a potassium iodide solution, and the liberated iodine was titrated with standard sodium thiosulphate solution. From the titration, the cobaltic content was determined. The cobalt was then extracted from the slurry and deposited electrolytically. Comparison of the results of the titration for cobaltic ion and the total cobalt deposited indicated that the separation was complete within the experimental error.

The specific activity of the cobaltic fraction was determined. The results of five experiments indicated that exchange was complete within 5% for times varying between one-half and one and one-half minutes. Exchange was thus virtually complete within the time required for the separation process.

IV. Investigation of Exchange between $\text{Co}(\text{NH}_3)_6^{++}$ and $\text{Co}(\text{NH}_3)_6^{+++}$

In ammoniacal solution, cobaltous ion is known (3) to form the hexammino cobaltous complex ion. Exchange between this and the radioactive hexammino cobaltic ion could conceivably occur by two different mechanisms. An electron transfer between the two ions would result in the appearance of activity in the complex of divalent cobalt, while the rapid and complete establishment of the equilibria



accompanied by an electron transfer between the cobaltous and cobaltic ions, would also lead to exchange.

Solutions 0.01 molar in radioactive hexammino cobaltic chloride and cobaltous chloride, and containing known concentrations of ammonia, were placed in sealed tubes under nitrogen to prevent oxidation of the divalent complex by atmospheric oxygen. After known periods of time at 25° C., the solutions were acidified and the divalent cobalt extracted and tested for radioactivity. In all cases, blank experiments were carried out, without the addition of divalent cobalt, to determine if decomposition of the cobaltic complex into extractable cobalt was occurring. The results of the experiments are given in Table III.

TABLE III
EXCHANGE BETWEEN $\text{Co}(\text{NH}_3)_6^{++}$ AND $\text{Co}(\text{NH}_3)_6^{+++}$ AT 25° C.

$M \text{ NH}_3$	Time, hr.	Apparent percentage exchange
3.6	3.5	0.19 ± 0.24
6.5	3.5	0.05 ± 0.13
6.0	24.0	0.03 ± 0.25
9.5	3.5	0.02 ± 0.07
6.0	336.0	3.2 ± 0.30
6.0	408.0	5.6 ± 0.51

Exchange is seen to be very slow, being about 6% complete at the end of a 17 day period. The blank experiments showed that in periods of less than one day, less than 0.1% of the complex decomposed, while in the 17 day period about 1.5% of the complex decomposed. Corrections have been made for this decomposition in the calculation of the percentage exchange.

Discussion

The slow rate of exchange between the cobaltous ion and the hexammino cobaltic ion in neutral solution, shown by the results of Table I, implies that either one or both of the processes represented by Reactions (1) and (2) are incompletely established under the conditions of these experiments.

That the process represented by Reaction (1), the dissociative equilibrium of the hexammino cobaltic ion, would lead to such a slow rate of exchange is shown by the results in Table II, where no exchange could be observed between the cobaltic ion and the complex in periods up to five hours. Owing to the instability of the cobaltic ion, it was not possible to carry out these experiments for the long periods of time used in the exchange experiments between the cobaltous ion and the complex, but the results clearly demonstrate that this exchange is only slowly established under the conditions which could be investigated.

The process represented by Reaction (2), the electron transfer between the uncomplexed cobaltous and cobaltic ions, has been found to be rapid when the two forms of cobalt are separated by precipitation of the cobaltic ion as potassium cobaltinitrite and also by chromatographic adsorption on alumina. It has not yet been established with certainty whether the observed exchange took place between the ions in solution or whether exchange was induced during the separation process. It was shown by a separate experiment that no exchange occurred between cobaltous ion and the cobaltinitrite ion when separation was achieved by precipitation of potassium cobaltinitrite, but there remains the possibility that exchange could have been induced during the formation of cobaltinitrite from cobaltic and nitrite ions. Also, during the separation by adsorption on alumina, exchange may have occurred on the surface of the adsorbent. Unless conditions are found where the rate of exchange is slow enough to be measurable, or where no catalysis is possible, the possibility exists that the observed exchange was induced during the separation process.

The results of Table III show that the exchange between the hexammino complexes of divalent and trivalent cobalt by electron transfer or the equilibria represented by Reactions (3) and (4) is slow. These equilibrium equations, representing the dissociation of the complexes in solution, are those which were assumed to occur by Lamb and Larson (3) in their potentiometric study of the instability constants of these complexes. They interpreted the potential of an electrode immersed in an ammoniacal solution containing both of these complexes as due to the $\text{Co}^{++} - \text{Co}^{+++}$ couple. The establishment of this potential implies an equilibrium involving an electron transfer between these ions on the surface of the electrode, according to the Nernst theory. The results reported here indicate that these equilibria are established only slowly in solution, at least in the absence of an electrode surface.

Acknowledgment

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KINETIC STUDIES OF THE HYDROLYSIS OF CYANOGEN HALIDES¹

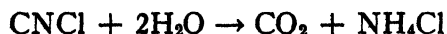
BY A. B. VAN CLEAVE, V. C. HASKELL,² J. H. HUDSON,
AND A. M. KRISTJANSON³

Abstract

The kinetics of the reaction between cyanogen chloride and water and between cyanogen bromide and water, catalyzed by hydrogen chloride or hydrogen bromide in dioxane solution, has been investigated. With stoichiometric proportions of cyanogen chloride and water, the reaction catalyzed by hydrogen chloride is of the second order, and the specific reaction rate is directly proportional to the square of the concentration of hydrogen chloride. This reaction was found to have zero temperature coefficient between 20° and 40° C. The reaction between cyanogen bromide and water, catalyzed by hydrogen bromide, has been shown to proceed through the formation of an unstable intermediate compound, which probably results from a primary reaction between cyanogen bromide and hydrogen bromide. The intermediate product was isolated but was so unstable that its identity was not satisfactorily established. The over-all hydrolysis reaction of cyanogen bromide has a positive temperature coefficient between 20° and 40° C. The catalyst in the hydrolysis of both cyanogen chloride and cyanogen bromide in dioxane solution appears to be molecular hydrogen chloride or hydrogen bromide rather than hydronium ions.

Introduction

Interest in the kinetics of the hydrolysis of cyanogen chloride arose from a study of the stability of crude cyanogen chloride by Van Cleave and Eager (9) and from a study of the hydrolysis and polymerization of cyanogen chloride by Van Cleave and Mitton (10). These authors had established that the hydrolysis of pure cyanogen chloride in the presence of hydrogen chloride proceeds quantitatively according to the equation:



but that the hydrolysis is accompanied by a polymerization reaction. It was not found possible to evaluate rate constants for the hydrolysis reaction from the rate of pressure increase, as the carbon dioxide formed dissolved appreciably in the unreacted liquid cyanogen chloride.

The present authors have found it possible to make kinetic studies of the hydrolysis reaction by using dioxane as an inert solvent. Cyanogen chloride, cyanogen bromide, hydrogen chloride, hydrogen bromide, and water are all quite soluble in dioxane, whereas ammonium halides are fairly insoluble. Hence, in this work, attempts have been made to study the rate of the acid catalyzed hydrolysis of both cyanogen chloride and cyanogen bromide by

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determining the amount of ammonium halide produced at various times for different initial concentrations of reactants and catalyst and at different temperatures.

Experimental

The Solubility of Ammonium Chloride and Ammonium Bromide in Dioxane-Water Mixtures

It was first necessary to establish the limiting water concentration in dioxane-water mixtures above which ammonium halides become appreciably soluble. This was done by determining how much of a known amount of ammonium halide could be recovered by filtration after the salt had been in contact with solutions of varying dioxane-water ratios for some length of time at 25° or 40° C. It was found that ammonium chloride is not appreciably soluble in dioxane-water mixtures containing up to 15 mole % of water at temperatures between 25° and 40° C. At water concentrations greater than 15 mole %, the solubility of ammonium chloride in the mixture increases sharply and eventually results in the separation of the mixture into two liquid phases (5).

Similar results were obtained for the solubility of ammonium bromide in dioxane - water - hydrogen chloride mixtures. No appreciable solubility of ammonium bromide was detected up to a water concentration of 0.677 molar. However, the solubility of ammonium bromide in dioxane - water - hydrogen bromide mixtures was greater and amounted to 0.0005 mole per liter in solutions which were 0.3 molar with respect to both water and hydrogen bromide at 25° C. (8). Since the initial concentration of water in some of the kinetic experiments was of the order of 0.3 molar, it is probable that some ammonium bromide escaped precipitation in the early parts of the run, although, as the reaction proceeds, the water is used up and the ammonium bromide becomes practically insoluble. In any case, the errors due to the loss of ammonium halides by solution in the reaction mixture are not large enough to introduce a gross error in the rate calculations.

The Rate of the Reaction $CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$ Catalyzed by Hydrogen Chloride in Dioxane Solution

Since ammonium chloride proved to be practically insoluble in solutions containing an excess of dioxane, it was possible to follow the course of the reaction by filtering off the precipitate and determining the amount of halide ion in it. Crude cyanogen chloride was purified by the method suggested by Douglas and Winkler (1) and the dioxane by the method of Fieser (2). For convenience in handling cyanogen chloride, a stock solution (1.5 to 2.5 molar) of it in dioxane was prepared. This stock solution was frequently standardized as follows. Five ml. of the stock solution was pipetted into a 100 ml. volumetric flask which contained 25 ml. of 1.5 *N* sodium hydroxide.

This solution was shaken and let stand for one-half hour to ensure that the hydrolysis represented by the equation



was complete. It was then diluted to 100 ml. with water, and a 50 ml. aliquot removed and back-titrated with 0.5 *N* sulphuric acid to a phenolphthalein end point. The molarity of the cyanogen chloride was calculated from the amount of alkali used in the hydrolysis reaction. As long as the stock bottle was kept tightly stoppered, the strength of the solution changed very slowly with time. Various standard solutions of hydrochloric acid of known density were used to provide the desired concentration of hydrogen chloride.

The general procedure in kinetic experiments was as follows. Ten milliliters of stock cyanogen chloride – dioxane solution was pipetted into a 100 ml. volumetric flask, which was then filled with dioxane to within about 5 ml. of the graduation mark. A calculated amount of standard hydrochloric acid was then added from a 1 ml. graduated pipette. The amount of acid solution to be added was determined by the amount of water required. The mixture was then diluted to 100 ml. with dioxane, and the flask stoppered and thoroughly shaken. The time of shaking was taken as zero time for the reaction. A number of 10 ml. samples of the reaction mixture were then transferred to previously prepared, clean, dry, 14 mm. diameter reaction tubes. These tubes were then cooled in an ice bath and their open ends sealed in a small flame, after which they were immersed in a constant temperature bath. Preliminary experiments had indicated that it was necessary to do these experiments in closed tubes as there was an appreciable loss of cyanogen chloride when rubber stoppered vessels were used. At intervals, the reaction tubes were opened and the contents run through a filter crucible under suction. Redistilled chloroform was used to wash all the ammonium halide into the filter crucible. The ammonium halide collected was dissolved in water and titrated with standard silver nitrate solution using dichlorofluorescein as an indicator.

The rate of the hydrolysis reaction was studied under three quite different ratios of the concentration of cyanogen chloride to water, as follows.

(a) Cyanogen Chloride and Water in Stoichiometric Proportions

Experiments were carried out with cyanogen chloride and water in stoichiometric proportions with varying concentrations of hydrogen chloride at temperatures of 20°, 30°, and 40° C. The reaction was found to be homogeneous in that the rate was not affected by increasing the glass surface or by adding additional amounts of solid ammonium chloride. Light had no effect on the rate of the reaction. By trial it was found, at least in the initial stages

of the reaction, that the results fitted a second order reaction rate curve as is illustrated for a typical experiment in Fig. 1, where $\frac{1}{a-x}$ (a = initial concentration of cyanogen chloride; x = amount of cyanogen chloride reacted

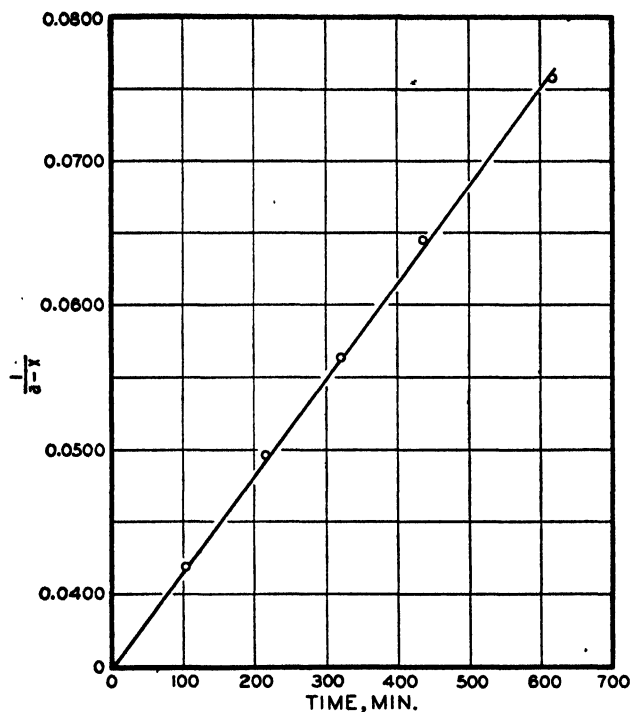


FIG. 1. $\frac{1}{a-x}$ vs. time in minutes for hydrolysis of cyanogen chloride at 20° C.

Cyanogen chloride and water in stoichiometric proportions
 a = initial concentration of cyanogen chloride,
 x = amount of cyanogen chloride reacted in time 't',
 Catalyst—Hydrogen chloride.

at time t , both in terms of their equivalent volume of standard silver nitrate solution) is plotted vs. the time t . Second order reaction rate constants were calculated from the slopes of such plots. A summary of the results obtained is given in Table I.

The dependence of the specific reaction rate for stoichiometric proportions of reactants on the concentration of the catalyst, hydrogen chloride, is shown by Fig. 2, where the rate constants at 20°, 30°, and 40° C. are plotted against the square of the molar concentration of hydrogen chloride. It was found by trial that such plots gave practically straight line relations. It was rather surprising to find that although the rate of the reaction was markedly affected by the concentration of hydrogen chloride, it was not appreciably changed when the temperature was varied from 20° to 40° C., that is, the reaction had practically a zero temperature coefficient.

TABLE I

SECOND ORDER SPECIFIC REACTION RATE FOR REACTANTS IN STOICHIOMETRIC PROPORTIONS

Catalyst: Hydrogen chloride

Temp., ° C.	Initial conc. of CNCl, moles/liter	Initial conc. of HCl, moles/liter	Specific reaction rate k , liters mole ⁻¹ min. ⁻¹
20	0.3162	0.0393	3.77×10^{-4}
	0.1932	0.0476	5.29×10^{-4}
	0.3162	0.0784	1.64×10^{-3}
	0.1932	0.0799	1.57×10^{-3}
	0.2038	0.1166	3.21×10^{-3}
	0.3162	0.1317	4.81×10^{-3}
	0.2415	0.1380	4.71×10^{-3}
	0.2898	0.1657	6.65×10^{-3}
	0.3162	0.1810	8.56×10^{-3}
30	0.1916	0.0473	4.28×10^{-4}
	0.1916	0.0799	1.44×10^{-3}
	0.1916	0.1093	3.04×10^{-3}
	0.2230	0.1276	3.97×10^{-3}
	0.2676	0.1528	6.53×10^{-3}
	0.3568	0.2040	1.03×10^{-2}
40	0.2357	0.0580	7.88×10^{-4}
	0.2401	0.0978	2.70×10^{-3}
	0.2401	0.1371	4.48×10^{-3}

Another method of determining the apparent order of a reaction is to determine the times, t_1 and t_2 , for definite fractions to react, starting with different initial concentrations, a_1 and a_2 . Using the time of half reaction for initial cyanogen chloride concentrations differing by 100%, but having the same initial concentration of hydrogen chloride, the reaction appeared to have an over-all order of approximately 2.

(b) *Cyanogen Chloride in Excess of Stoichiometric Proportions*

To determine the apparent order of the reaction with respect to the concentration of water, experiments were performed in which the initial amount of cyanogen chloride was about eight times that required to react with all of the water, so that the concentration of cyanogen chloride could be considered practically constant throughout the course of the reaction. Actually, when the concentration of water had undergone about a 40% change, the cyanogen chloride concentration had changed by about 5%. Measurements were therefore restricted to the first third of the reaction. The experimental procedure was the same as that outlined above. Again it was found that when the function $\frac{1}{a-x}$ (where a = the initial concentration of water and x = amount of water reacted at time t , both in terms of milliliters of standard silver nitrate solution) was plotted against the time t ,

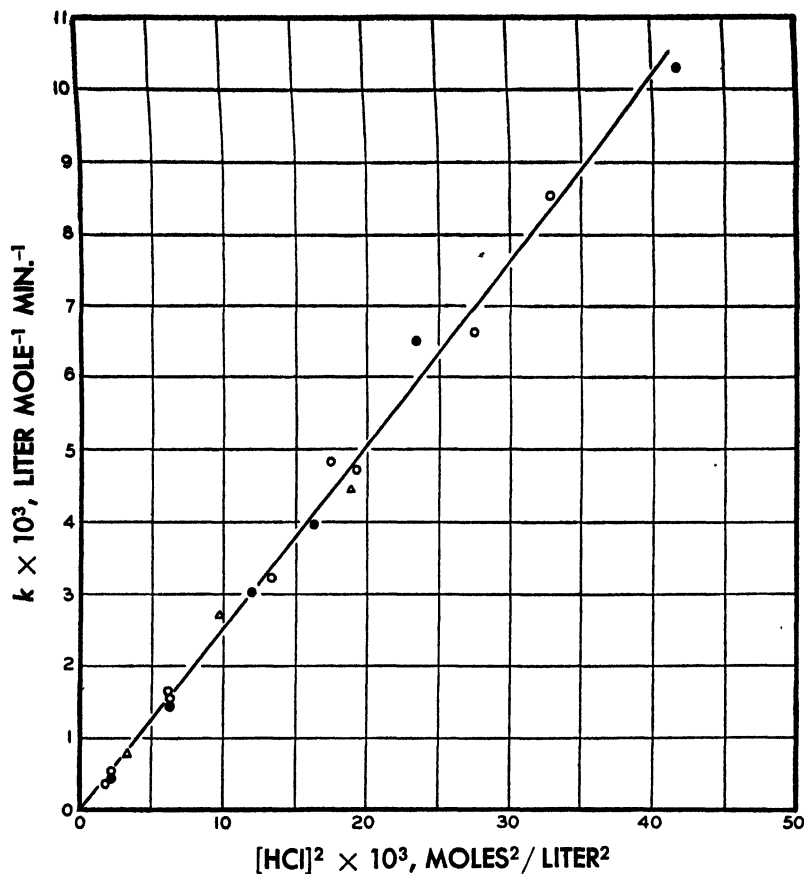


FIG. 2. Dependence of specific reaction rate on the concentration of hydrogen chloride.

Cyanogen chloride and water in stoichiometric proportions

○ Experiments at 20° C.

● Experiments at 30° C.

△ Experiments at 40° C.

reasonably straight lines were obtained, at least in the initial stages of the reaction. Second order specific reaction rates were calculated from the slopes of such plots. The results are summarized in Table II.

The dependence of the second order specific reaction rate k on the concentration of hydrogen chloride is shown in Fig. 3. Again it was found that within experimental error, a plot of k vs. the square of the hydrogen chloride concentration gave a straight line, regardless of the temperature. That is, there was no evidence for a temperature coefficient. This is in contrast to the results of Van Cleave and Mitton (10), who found the hydrolysis of cyanogen chloride in the absence of dioxane to possess a definite positive temperature coefficient.

Using the times for one-third of the water to react for initial concentrations of water differing by 100% also indicated that the reaction was apparently second order with respect to water when cyanogen chloride was present in excess.

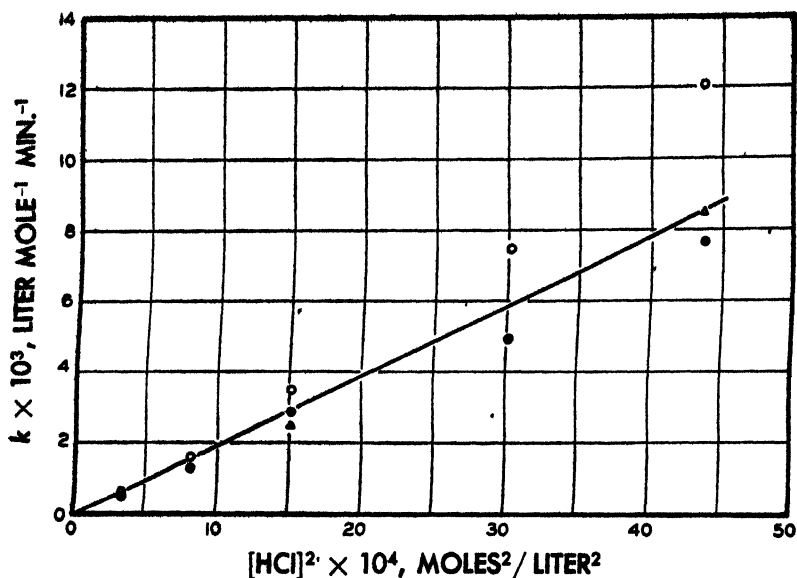


FIG. 3. Dependence of specific reaction rate on the concentration of hydrogen chloride.

Cyanogen chloride present in excess

○ Experiments at 20° C.

● Experiments at 30° C.

△ Experiments at 40° C.

TABLE II

SECOND ORDER SPECIFIC REACTION RATE WITH CYANOGEN CHLORIDE IN EXCESS

Initial conc. of water in all cases = 0.317 mole/liter

Temperature, ° C.	Initial conc. of CNCl, moles/liter	Conc. of HCl, moles/liter	Specific reaction rate k , liters mole ⁻¹ min. ⁻¹
20	1.291	0.0184	6.13×10^{-4}
		0.0284	1.60×10^{-3}
		0.0390	3.52×10^{-3}
		0.0550	7.43×10^{-3}
		0.0660	1.20×10^{-2}
30	1.157	0.0184	5.66×10^{-4}
		0.0284	1.28×10^{-3}
		0.0390	2.84×10^{-3}
		0.0550	4.95×10^{-3}
		0.0660	7.66×10^{-3}
40	1.291	0.0390	2.47×10^{-3}
		0.0660	8.44×10^{-3}

(c) Water in Excess of Stoichiometric Proportions

Attempts were made to study the rate of the reaction in the presence of excess water. In this case, a different experimental procedure had to be used,

as the ammonium chloride formed dissolved in the water. A number of different methods of determining the extent of the reaction were tried but none of them proved satisfactory. Methods tried were:

(1) Determination of NH_4^+ by the conventional method of adding excess sodium hydroxide and distilling the ammonia into standard acid. This method failed because cyanogen chloride itself reacted in basic solution to give a cyanate which hydrolyzed further to produce ammonia.

(2) Determination of NH_4^+ gravimetrically by precipitation as the chloroplatinate. The salt proved too soluble in aqueous solutions of cyanogen chloride to make the method useful.

(3) Volumetric determination of chloride by titration with standard silver nitrate solution, a correction being applied for the known amount of hydrogen chloride present. Difficulty was experienced in obtaining a satisfactory end point and tests indicated that this was probably due to slow reaction of cyanogen chloride with silver nitrate to give silver chloride. This is in accord with the observations of Zappi (12), but at variance with the experience of Douglas and Winkler (1).

(4) Determination of the cyanogen chloride concentration using the method previously described for standardizing cyanogen chloride - dioxane solutions. A number of experiments were carried out with cyanogen chloride in aqueous solution at various concentrations of hydrogen chloride. With an initial concentration of cyanogen chloride of 0.255 mole per liter and hydrogen chloride concentration of 1.5 moles per liter, the reaction was found to be very slow, and the results of analyses in both sealed and stoppered vessels were so erratic that they were of little value in determining the rate of the reaction.

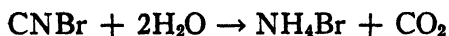
As yet the authors have not succeeded in developing a satisfactory method of following the course of the acid catalyzed hydrolysis of cyanogen chloride in aqueous solution. It does appear, however, that the rate of the reaction for equal concentrations of hydrogen chloride is much less in the presence of excess water than it is when there is a large excess of dioxane present. This suggests that the effective catalyst is probably molecular hydrogen chloride rather than hydronium ions. Krieble and Peiker (7), in studying the hydrolysis of hydrogen cyanide in the presence of hydrogen chloride, also concluded that the effective catalyst was undissociated hydrogen chloride.

The Rate of the Reaction $\text{CNBr} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{NH}_4\text{Br}$ Catalyzed by Hydrogen Chloride and Hydrogen Bromide in Dioxane Solution

A systematic study of the factors affecting the rate of the hydrolysis of cyanogen bromide, catalyzed by hydrogen halides in dioxane solution, was undertaken to see if the reaction was similar to that undergone by cyanogen chloride.

Cyanogen bromide was prepared and purified (4) and a stock solution of it (approximately 1 molar) in dioxane was standardized by an iodometric method. Unlike cyanogen chloride, cyanogen bromide liberates iodine quantitatively from an iodide in acid solution and can therefore be conveniently determined by this method. A constant boiling mixture of aqueous hydrogen bromide was used as catalyst in some experiments, while in others a standardized solution of gaseous hydrogen bromide in dioxane was used.

It was necessary to determine that the over-all hydrolysis of cyanogen bromide proceeds in a manner analogous to that of cyanogen chloride to produce an ammonium halide and carbon dioxide. It is known that cyanogen bromide reacts slowly with water to give hydrobromic and cyanic acids (11), and that cyanic acid reacts with water to give ammonia and carbon dioxide, thus giving an over-all reaction represented by



if it occurs in an acid medium. The completeness of this reaction was determined by placing a known amount of cyanogen bromide and hydrogen bromide in a reaction vessel with sufficient water for the reaction to go to completion. The amount of ammonium halide formed indicated that the reaction was virtually complete as written above.

In preliminary experiments it was found that the reaction in aqueous solution, even with a concentration of hydrogen chloride as high as 1.2 molar, was too slow to be practicable for kinetic studies. However, in dioxane solutions with initial concentrations of water from 0.1 to 0.4 molar, the reaction proceeded at an appreciable rate using either hydrogen chloride or hydrogen bromide as a catalyst.

The general procedure followed was similar to that described above for cyanogen chloride except that the filtrate, after removal of the ammonium halide, was retained and the amount of unreacted cyanogen bromide determined iodometrically. In this way, the amount of halide formed and the amount of cyanogen bromide reacted at any time were simultaneously determined. The reaction appeared to be homogeneous, as its rate was not affected by increasing the glass surface or by the addition of solid ammonium halides.

All the experiments showed the same general characteristics. In the initial stages of the reaction, the concentration of cyanogen bromide decreased more rapidly than the amount of ammonium halide increased, and it was only after the reaction had been in progress for a considerable time that the total moles of unreacted cyanogen bromide plus the moles of ammonium halide formed began to approach the initial number of moles of cyanogen bromide present. This is a good indication that an unstable intermediate product was formed. If it is assumed that the concentration of the intermediate product is equal to the difference between the sum of the unreacted cyanogen bromide plus the ammonium halide formed and the original concentration of cyanogen

bromide, a curve for the concentration of the intermediate vs. time can be constructed. Fig. 4 shows the results of a typical experiment, the dotted line representing the theoretical concentration of the intermediate product.

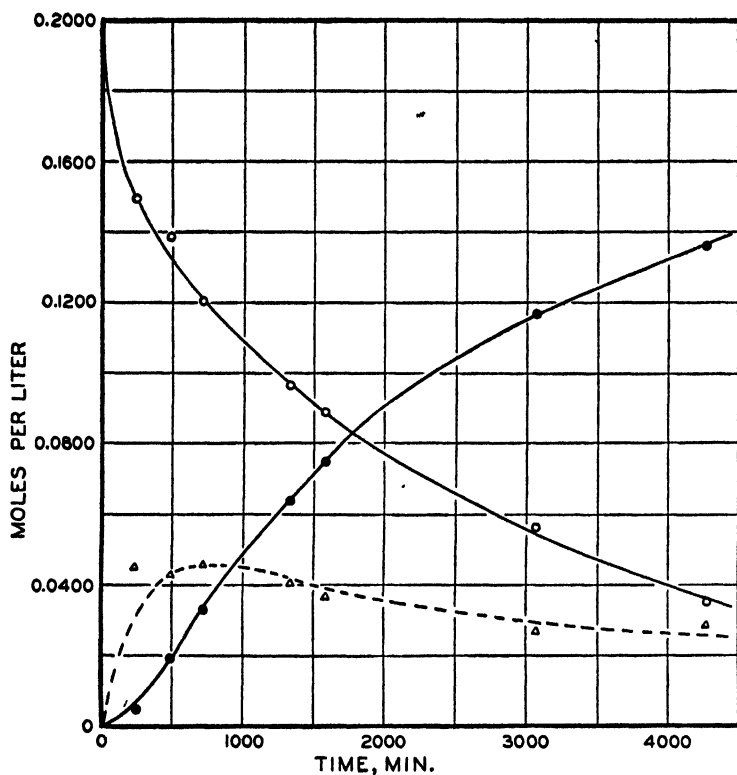


FIG. 4. Variation of the concentration of cyanogen bromide, ammonium halide, and intermediate compound with time.

- Concentration of CNBr,
- Concentration of NH₄X,
- △ Concentration of intermediate compound.

In dioxane solution, hydrogen chloride proved to be a much better catalyst than hydrogen bromide for equal molar concentrations. These relative catalytic effects are in agreement with those of Krieble and McNally (6) on the acid catalyzed hydrolysis of hydrogen cyanide. The decrease of catalytic activity of hydrogen chloride in aqueous solution indicates that the catalytic agent is probably molecular hydrogen chloride rather than hydronium ions. Also, since hydrochloric and hydrobromic acids have approximately the same hydronium ion concentration at the same molarity, it seems certain that the principal catalyst is not hydronium ions. That the effective catalyst is molecular hydrogen chloride or hydrogen bromide is also supported by the fact that the rate of disappearance of cyanogen bromide for a given catalyst concentration decreased as the amount of water initially present in the dioxane solution was increased. This fact introduced a fundamental difficulty into the kinetic studies, as the effective concentration of the catalyst was influenced

by the amount of water present. A similar circumstance has been noted by Hantzsch (3), who found that the catalytic activity of sulphuric acid for the conversion of nitriles to acid amides was greatly decreased by increasing the water content.

The variation of the catalytic effect with increasing concentration of acid is shown by the results in Table III for experiments at 25° C. with approximately the same initial concentrations of cyanogen bromide and water. The

TABLE III

VARIATION OF THE TIME OF HALF REACTION OF CYANOGEN BROMIDE WITH THE INITIAL CONCENTRATION OF HYDROGEN BROMIDE AT 25° C.

Initial conc. of CNBr, moles/liter	Initial conc. of H ₂ O, moles/liter	Initial conc. of HBr, moles/liter	$t_{\frac{1}{2}}$ min.
0.1513	0.300	0.0500	16,000
0.1502	0.300	0.1000	2,440
0.1459	0.300	0.1500	1,400
0.1410	0.300	0.2000	710

time for half the initial cyanogen bromide to react was determined by plotting the cyanogen bromide concentration vs. the time and drawing a smooth curve through the experimental points.

Assuming that the decrease in the cyanogen bromide concentration is due to a reaction between cyanogen bromide and hydrogen bromide, the large increase in the rate of the reaction, observed by doubling the concentration of hydrogen bromide, would mean that the rate depends on the concentration of hydrogen bromide to some power greater than 1, or, that the measured molar concentration of hydrogen bromide is not the same as its effective concentration. The amount of molecular hydrogen bromide in solution at any time is determined by the amount of water present and the ionization constant of the acid. If the initial step in the hydrolysis is a reaction between cyanogen bromide and molecular hydrogen bromide, the rate of disappearance of cyanogen bromide would be expected to decrease with increasing initial concentration of water for constant amounts of hydrogen bromide, and to increase with increased concentration of hydrogen bromide at a constant concentration of water, as was observed in these experiments.

When the rate of decrease of the cyanogen bromide concentration or the rate of increase of ammonium halide was investigated, it was evident that the apparent order of the reaction changed as the reaction proceeded. This is another indication that a number of consecutive reactions are involved before the final products are produced. However, it was observed that the initial rate of disappearance of cyanogen bromide (i.e., up to about one-third reaction) followed a second order kinetic law when it was assumed that the initial

reaction was one between cyanogen bromide and hydrogen bromide. This is illustrated in Fig. 5 where the function $\log \frac{b(a-x)}{a(b-x)}$ is plotted against time for typical experiments at 25° and 35° C. (a is the initial concentration of cyanogen

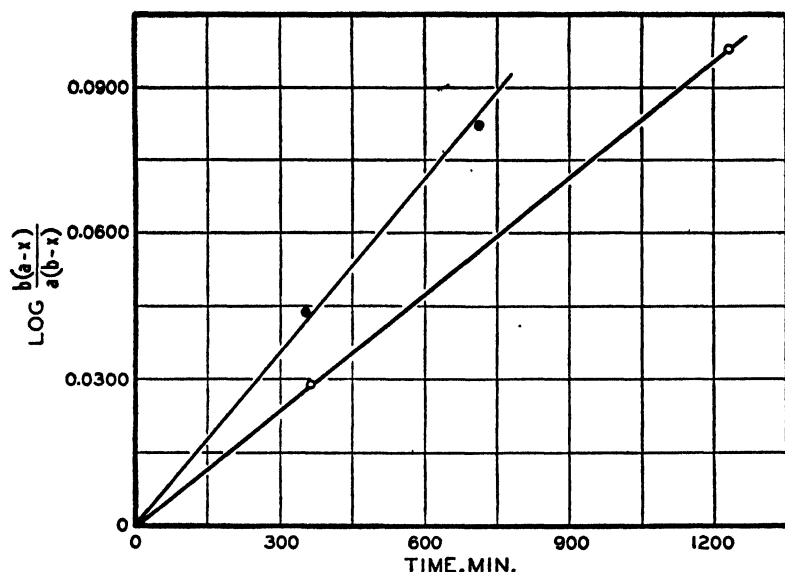


FIG. 5. $\log \frac{b(a-x)}{a(b-x)}$ vs. time in minutes for initial stage of reaction between cyanogen bromide and hydrogen bromide in dioxane.

- Experiments at 25° C.
● Experiments at 35° C.

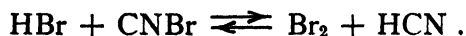
bromide and b is the initial concentration of hydrogen bromide; $a - x$ is the concentration of cyanogen bromide at time t and $b - x$ is the concentration of hydrogen bromide at time t on the assumption that hydrogen bromide is used up at the same rate as the cyanogen bromide.) The initial concentration of water in these experiments was the same at approximately twice the molar concentration of cyanogen bromide. One would not expect the reaction to continue to follow a second order law beyond the initial stages, as the hydrogen bromide must be regenerated in subsequent steps, and the concentration of molecular hydrogen bromide also changes as the water in the reaction mixture is used up.

Attempts were made to study the over-all order of the reaction with respect to the concentration of cyanogen bromide by keeping the initial concentrations of water and acid catalyst constant while varying that of cyanogen bromide, but rather inconsistent results were obtained. However, when the initial concentrations of cyanogen bromide and water were maintained constant while that of the hydrogen bromide was varied, the results indicated the over-all reaction to be second order with respect to the concentration of hydrogen bromide. This result is in agreement with the observed effect of hydrogen chloride concentration on the rate of hydrolysis of cyanogen chloride.

It is evident from Fig. 5 that the rate at which cyanogen bromide disappeared in these experiments was definitely increased when the temperature was raised from 25° to 35° C. This is in marked contrast to the experiments with cyanogen chloride where no temperature coefficient was found. When second order specific reaction rates were calculated from the slopes of the lines in Fig. 5 and substituted into the Arrhenius equation, an apparent activation energy of 8400 cal. per mole was obtained for the proposed initial step of the reaction.

Interfering Side Reactions

When a hydrogen bromide-dioxane solution was added to a solution of cyanogen bromide in dioxane, a light yellow color developed almost immediately. When hydrogen chloride was added to cyanogen bromide in dioxane, a similar yellow color developed in about 10 min. The yellow color was apparently caused by the formation of some free bromine, as it could be extracted with either carbon tetrachloride or carbon disulphide, and the color in the carbon tetrachloride layer could be discharged by the addition of a few drops of amylene. A small concentration of bromine could possibly arise from the establishment of the equilibrium



In experiments which were allowed to proceed until virtually all of the cyanogen bromide was hydrolyzed, the yellow color finally disappeared, as would be expected if the above equilibrium had been established. There was no evidence that the amount of bromine produced was appreciable, hence the effect of this side reaction was not considered to be important.

Possible reactions between cyanogen bromide and dioxane and between hydrogen bromide and dioxane were considered. It was found that solutions of cyanogen bromide in dioxane were stable over long periods of time, but that solutions of dry hydrogen bromide in dioxane showed a steady decrease of hydrogen bromide with time even when the container was tightly stoppered. However, when water was present in amounts comparable to those used in the hydrolysis experiments, the rate of disappearance of hydrogen bromide was much slower and probably was not rapid enough to seriously affect its concentration during the course of a hydrolysis experiment. It would be desirable, however, to investigate further the reaction between hydrogen bromide and dioxane.

Intermediate Products in the Hydrolysis of Cyanogen Bromide and Cyanogen Chloride

Kinetic studies on the hydrolysis of cyanogen bromide catalyzed by hydrogen chloride or hydrogen bromide indicated that an unstable intermediate product was formed, probably as a result of a primary reaction between cyanogen bromide and the hydrogen halide. Hence, attempts were made to prepare and isolate possible intermediate compounds.

In a preliminary experiment, 100 ml. of hydrogen bromide – dioxane solution (1 molar) was added to 40 ml. of cyanogen bromide – dioxane solution (2.5 molar) in a glass stoppered bottle. The mixture immediately turned a deep orange-brown color and the contents of the bottle became warm. On cooling and shaking, a solid began to settle out. The solid was removed by filtration under suction and washed with dioxane. The product was a light yellow, feathery solid which fumed strongly on exposure to moist air. It melted at 98° C. and dissolved readily in water, with the evolution of a gas, to give an acidic solution with a strong odor of cyanogen bromide. It was soluble in excess dioxane, giving a yellow colored solution. When additional dioxane containing a small amount of water was added to a solution of the product in dioxane, a white solid precipitated out slowly. This solid proved to be ammonium bromide.

Systematic experiments were carried out in an attempt to isolate and analyze any possible compounds that might be formed between hydrogen halides and cyanogen halides. In these experiments, the gaseous hydrogen halide was passed over phosphorus pentoxide into the pure liquid cyanogen halide or the cyanogen halide in various solvents. Table IV is a summary of the results obtained.

TABLE IV

THE FORMATION OF COMPOUNDS BETWEEN HYDROGEN HALIDES AND CYANOGEN HALIDES

Hydrogen halide	Cyanogen halide	Result
HCl	CNCl (liquid)	Polymerization of CNCl
HBr	CNBr (liquid)	Polymerization of CNBr
HCl	CNCl in dioxane	Light yellow colored solution, no precipitate
HBr	CNCl in dioxane	Reddish-orange colored solution, light yellow colored precipitate formed
HCl	CNBr in dioxane	Reddish-orange colored solution, no precipitate
HBr	CNBr in dioxane	Reddish-orange colored solution, light yellow colored precipitate—not polymer
HBr	CNBr in benzene	Orange colored solution, white precipitate
HBr	CNBr in carbon tetrachloride	Reddish-orange colored solution, precipitate formed

Except in the cases where the cyanogen halide polymerized, the solid products proved to be rather unstable, and no successful analyses were obtained. When attempts were made to dry the compound formed between hydrogen bromide and cyanogen bromide by maintaining it in a vacuum desiccator under reduced pressure, it was found that the nitrogen analysis (Kjeldahl) varied with the length of the aspiration period, showing a steady

increase from about 6% (one hour aspiration) to 13.4% (48 hr. aspiration). The melting point of the substance increased with drying up to a maximum of 105° C. and then decreased to 67° C. as the nitrogen content increased. The product seemed to gradually revert to cyanogen bromide (13.2% nitrogen, melting point 52° C.).

Similar analyses were done on the product formed by the action of hydrogen bromide on cyanogen chloride in dioxane and the results were much the same. The melting point was initially about 105° C. but it declined with continuous aspiration while the nitrogen percentage increased. This product closely resembled that formed between hydrogen bromide and cyanogen bromide in dioxane in appearance, smell, and reactions, but it is not certain that they were the same.

The products formed between hydrogen bromide and cyanogen bromide in benzene and carbon tetrachloride did not appear to be the same as that formed in dioxane solution.

There is no doubt that compounds between hydrogen bromide and cyanogen bromide and between hydrogen chloride and cyanogen bromide are formed in dioxane solution, but considerably more work will have to be done before these unstable products can be identified.

Discussion

This work strongly indicates that the catalytic effect of hydrogen chloride or hydrogen bromide on the rate of hydrolysis of cyanogen chloride or cyanogen bromide in dioxane solution is not due to hydronium ions but rather to the molecular hydrogen halide. At least in the case of the hydrolysis of cyanogen bromide in dioxane it has been fairly definitely established that the primary reaction is the formation of a compound between cyanogen bromide and the hydrogen halide. However, the possibility that the solvent is part of these compounds has not been excluded.

No definite evidence for the formation of a compound between hydrogen chloride and cyanogen chloride in dioxane solution was obtained, but this may be because such an intermediate is even less stable than that formed between cyanogen bromide and hydrogen bromide. In an investigation of the mechanism of the conversion of nitriles to acid amides, Hantzsch (3) prepared several compounds of the type $\text{RCN} \cdot n\text{HX}$. While none of these compounds was very stable, he found that the hydrochlorides were the least stable, while the hydroiodides were the most stable. He also found that the solvent had some influence on the type of compound that was formed, as was noted in the present work. It appears, then, that it is not unreasonable to suppose that a compound between hydrogen chloride and cyanogen chloride might not be as stable as one formed between hydrogen bromide and cyanogen bromide. The fact that hydrogen chloride was observed to have a greater accelerating effect than hydrogen bromide on the rate of the over-all hydrolysis of cyanogen

bromide may be taken as a further indication that intermediate hydrochlorides are less stable than hydrobromides, that is, the hydrochloride intermediates react more rapidly with water.

Assuming that the initial step in the hydrolysis of cyanogen chloride is a reaction between cyanogen chloride and hydrogen chloride, the kinetic experiments indicate that this initial reaction is probably not a simple bimolecular process, that is, probably more than one molecule of hydrogen chloride is involved in the intermediate. The subsequent reaction of the intermediate with water to form ammonium chloride and carbon dioxide is probably more rapid than the initial intermediate forming reaction or reactions.

A suggested explanation for the absence of a temperature coefficient in the cyanogen chloride reaction is that there is an equilibrium established between the intermediate product and the original reactant. If this intermediate product were to become less stable with increasing temperature, dissociating into its reactants, then the decrease in its concentration might be sufficient to balance the normal increase of the rate of its reaction to give the final products.

The authors do not feel justified in proposing detailed mechanisms for the reactions investigated as the systems are obviously very complex and the identity of the intermediate compounds has not been established.

Acknowledgment

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ÉTUDE DE LA SYNTHÈSE DE LA PROLINE PAR CYCLISATION D'UN ACIDE VALÉRIANIQUE DIHALOGÉNÉ¹

PAR ROGER GAUDRY ET LOUIS BERLINGUET

Résumé

Les acides α,δ -dibromovalérianique, α -bromo- δ -chlorovalérianique, α -chloro- δ -bromovalérianique et α,δ -dichlorovalérianique ont été préparés dans le but de les cycliser par l'ammoniaque, pour obtenir la proline. Ils ont été synthétisés à partir du δ -chlorovaléronitrile ou de l'aldéhyde δ -hydroxyvalérianique. L'hydrolyse alcaline du δ -chlorovaléronitrile a donné l'acide δ -hydroxyvalérianique, qui a aussi été obtenu par oxydation de l'aldéhyde δ -hydroxyvalérianique. L'acide δ -hydroxyvalérianique a été traité par l'acide bromhydrique pour donner l'acide δ -bromovalérianique, qui a été bromé ou chloré en position α . L'hydrolyse acide du δ -chlorovaléronitrile a donné l'acide δ -chlorovalérianique, qui a aussi été bromé ou chloré en position α . Les cyclisations des acides α -bromo- δ -chlorovalérianique, α,δ -dibromovalérianique, α,δ -dichlorovalérianique et α -chloro- δ -bromovalérianique effectuées à une température de 70° C. ont donné respectivement des rendements de 40%, 25%, 25% et 10% en proline, isolée sous forme de sel de cuivre. Une température plus élevée pour la cyclisation ne donne pas d'augmentation appréciable des rendements.

Introduction

Willstätter a synthétisé la proline (XI) pour la première fois, en cyclisant l'ester éthylique de l'acide α -carbéthoxy- α,δ -dibromovalérianique par l'ammoniaque (12). Plusieurs autres synthèses ont depuis été réalisées. Cependant, aucune ne semble satisfaisante, soit à cause de difficultés de manipulations, soit à cause des faibles rendements obtenus ou de la difficulté de se procurer les produits de départ.

Plusieurs auteurs, en particulier Fischer (3) et Suzuki (4), Frankel (6) et Willstätter (13) ont repris la cyclisation de dérivés de l'acide α,δ -dibromovalérianique, et ont obtenu la proline avec des rendements de l'ordre de 20 à 40%. Récemment, Paul a réalisé la même synthèse en se servant de l'ester méthylique de l'acide α,δ -dichlorovalérianique (10), mais sans mentionner de rendement. Il en a aussi préparé l'amide, mais il ne semble pas avoir obtenu l'acide libre.

Nous avons pensé qu'il serait intéressant d'étudier de façon systématique la cyclisation des acides dihalogénés libres, pour savoir si la cyclisation d'acides dihalogénés autres que l'acide α,δ -dibromovalérianique peut donner des rendements supérieurs à ceux obtenus par Willstätter. Dans ce but, nous avons préparé les quatre acides dihalogénés suivants: α,δ -dibromovalérianique (VII), α -bromo- δ -chlorovalérianique (IX), α,δ -dichlorovalérianique (X) et α -chloro- δ -bromovalérianique (VIII). A notre connaissance, seul l'acide, α,δ -bromovalérianique (VII) était déjà décrit dans la littérature (1, 4, 9, 10,

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12). Willstätter l'avait préparé en condensant le malonate d'éthyle avec le bromure de triméthylène (12). Mais cette condensation ne se fait qu'avec un faible rendement. Récemment, Fling *et al.* l'ont obtenu avec un rendement de 10% à partir de la cyclopentanone (5). Paul n'a obtenu que 40% d'acide dibromovalérianique (VII) par ouverture de l'acide tétrahydropyromucique au moyen de l'acide bromhydrique (10). Ces rendements peu élevés nous ont incités à préparer l'acide dibromovalérianique (VII) en partant de produits plus facilement accessibles, comme l'aldéhyde δ -hydroxyvalérianique (IV) et le δ -chlorovaléronitrile (II).

Par hydrolyse acide du δ -chlorovaléronitrile (II), nous avons obtenu l'acide δ -chlorovalérianique (III) avec un rendement de 73%. L'addition de brome, en présence de phosphore, d'après la méthode de Merchant (9) nous a donné l'acide α -bromo- δ -chlorovalérianique (IX) avec 93% de rendement. En substituant le chlore au brome, nous avons obtenu l'acide α,δ -dichlorovalérianique (X) avec des rendements variant de 83% à 88%.

L'emploi de chlorure de sulfuryle comme agent de chloruration, en présence de trichlorure de phosphore, avec irradiation du mélange au moyen d'une lampe à vapeur de mercure, a donné aussi l'acide α,δ -dichlorovalérianique (X), bien qu'avec un rendement de 72%. L'action directe du chlorure de sulfuryle sur le δ -chlorovaléronitrile (II), suivie d'hydrolyse, a donné un mélange de 38% d'acide α,δ -dichlorovalérianique (X) et de 27% d'acide δ -chlorovalérianique (III). Ces rendements indiquent que la molécule de l'acide δ -chlorovalérianique est relativement inerte vis-à-vis le chlorure de sulfuryle, mais il demeure possible qu'une activation plus efficace ou plus prolongée permette d'améliorer le rendement.

Par hydrolyse alcaline du δ -chlorovaléronitrile (II), nous avons obtenu 84% d'acide δ -hydroxyvalérianique (V). Nous avons aussi préparé cet acide par oxydation de la δ -hydroxyvaléraldéhyde (IV) au moyen du permanganate de potassium en milieu alcalin.

Nous avons alors traité l'acide δ -hydroxyvalérianique (V) par l'acide bromhydrique à 48% et nous avons obtenu l'acide δ -bromovalérianique (VI) avec 53% de rendement. La bromuration et la chloruration en α nous ont donné respectivement 87% d'acide α,δ -dibromovalérianique (VII) et 82% d'acide α -chloro- δ -bromovalérianique (VIII).

Les quatre acides dihalogénés ont été cyclisés en proline (XI) par chauffage sous pression avec un excès d'ammoniaque concentrée à 70° C. pendant 48 h., ainsi qu'à 130° C. pendant une heure.

On trouvera dans le tableau I, les rendements en proline obtenus dans chaque cas.

Il est remarquable de constater que les meilleurs rendements ont été obtenus à partir de l'acide α -bromo- δ -chlorovalérianique, tandis que l'acide α -chloro- δ -bromovalérianique n'a donné qu'un très mauvais rendement en proline.

TABLEAU I.

Acide dihalogéné	P. é., °C.	n_D^{20}	% d'halogènes		% de proline	
			Calc.	Trouvé	70° C.	130° C.
α, δ -Dibromovalérianique*	168-172 (14 mm.)	1.535	61.5	60.0	23-25	23-25
α -Chloro- δ -bromovalérianique	170-175 (21 mm.)	1.515	53.6	53.9	8-12	10-15
α -Bromo- δ -chlorovalérianique	165-170 (17 mm.)	1.515	53.6	52.0	38-42	40-45
α, δ -Dichlorovalérianique	160-162 (21 mm.)	1.488	41.5	40.8	21-25	21-25

* *Références (1, 4, 9, 10, 12).*

Comme on pouvait le prévoir, les acides dibromo et dichlorovalérianiques ont donné à peu près le même rendement, nettement inférieur toutefois à celui obtenu à partir de l'acide α -bromo- δ -chlorovalérianique.

De plus, il ne semble pas y avoir avantage à effectuer cette cyclisation à une température très élevée. Les rendements obtenus à 130° C. n'ont jamais été notablement supérieurs et ont parfois été légèrement inférieurs à ceux obtenus à 70° C. Quelques essais effectués à 160° C. n'ont pas non plus permis d'améliorer les rendements, quelle qu'ait été la durée du chauffage.

Ces résultats indiquent que l'atome d'halogène le plus facilement substituable doit être en position α , pour que la cyclisation donne un rendement convenable. Par contre, lorsque l'atome d'halogène le plus actif est placé en position δ , les rendements en proline sont très mauvais. Et lorsque les deux atomes d'halogènes sont identiques dans la même molécule, les rendements sont sensiblement les mêmes, quel que soit l'halogène.

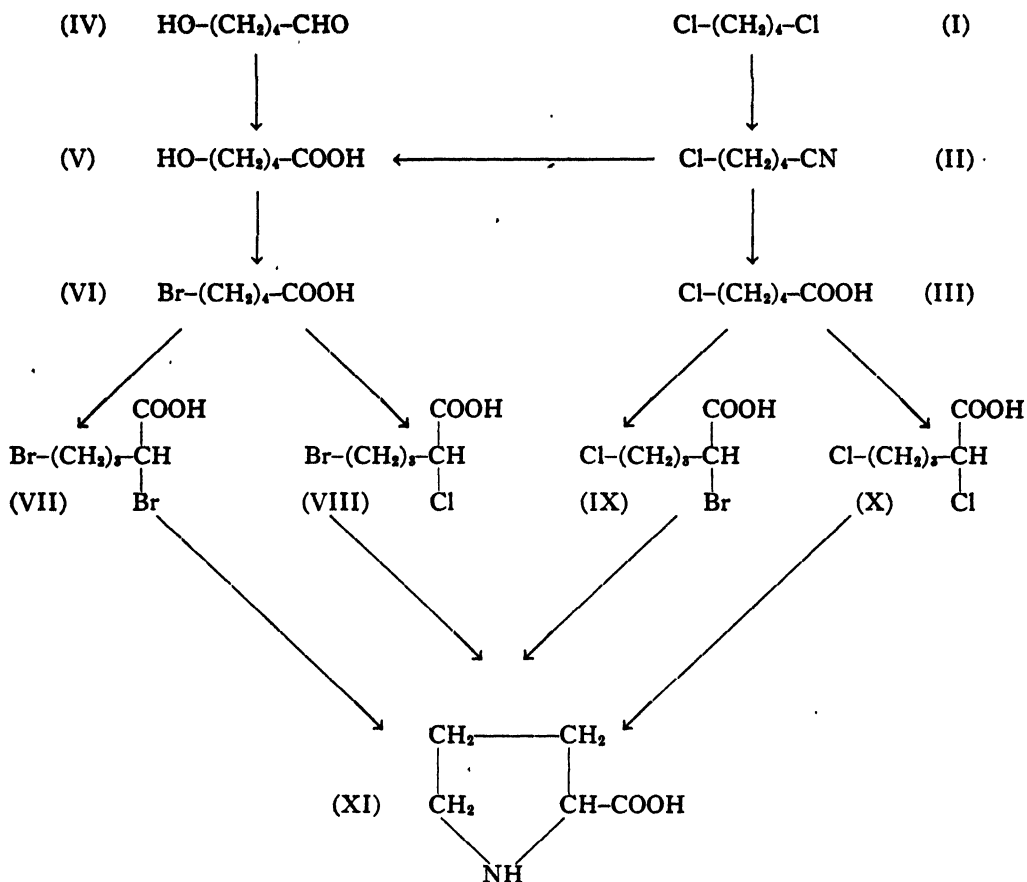
Il semble donc que l'on doive s'attendre à obtenir un meilleur rendement en proline par cyclisation de l'acide α -amino- δ -chloro ou δ -bromovalérianique, que par cyclisation de l'acide δ -amino- α -chloro ou α -bromovalérianique.

Cette hypothèse est déjà en partie confirmée par les résultats antérieurs de Fischer (3) qui n'a obtenu qu'un rendement de 23% en proline à partir de l'ester éthylique de l'acide α -carbéthoxy- α -bromo- δ -phtalimidovalérianique, tandis que Gaudry (8) a obtenu 35% de proline à partir de l'acide α -amino- δ -hydroxyvalérianique par l'intermédiaire de l'acide α -amino- δ -bromovalérianique. De plus, Sørensen et Andersen (11) prétendent avoir obtenu un rendement très élevé en proline à partir de l'ester éthylique de l'acide α -carbéthoxy- α -phtalimido- δ -bromovalérianique.

Une étude préliminaire a été entreprise dans le but de déterminer la nature des résidus de cyclisation. Ces résidus donnent des sels de cuivre très solubles dans l'eau, solubles dans l'alcool, non cristallisables, avec une teneur en azote presque identique au sel de cuivre de la proline. Ils donnent aussi avec un excès d'acide picrique une masse cristalline assez soluble dans l'eau froide et se décomposant vers 210° C.

Comme ces résidus ne semblent contenir aucune trace d'ornithine, ainsi que le démontre la solubilité des picrates, il est donc probable qu'ils sont

formés d'acides aminés complexes renfermant deux restes d'acide valériannique ou plus par molécule.



Partie expérimentale

Acide δ -chlorovalériannique (III)

Dans un ballon d'un litre, on place 117.5 g. de δ -chlorovaléronitrile (1.0 mole), 200 ml. d'acide chlorhydrique, 200 ml. d'acide formique et 200 ml. d'eau distillée. On fait bouillir le mélange à reflux pendant quatre heures. Après refroidissement, on extrait à l'éther, on sèche la solution étherée sur du sulfate de sodium anhydre, on évapore l'éther et on se débarrasse des sels résiduels en filtrant à succion. Par distillation dans le vide, on obtient l'acide δ -chlorovalériannique. Rendement: 100.0 g., 73.3%. P. é. 138° à 140° C. à 10 mm. Litt.: 141° à 149° C. à 12 mm. (1). Indice de réfraction: n_D^{20} 1.458. Calculé pour $\text{C}_5\text{H}_9\text{O}_2\text{Cl}$: Cl, 25.9%. Trouvé: Cl, 25.5%.

Acide α -bromo- δ -chlorovalériannique (IX)

Dans un ballon muni d'un réfrigérant, on place 54.6 g. d'acide δ -chlorovalériannique (0.4 mole), 1.5 g. de phosphore rouge et 80 g. de brome liquide (1.0 mole). On chauffe le ballon au bain-marie à environ 75° C. pendant

seize heures. Puis on porte la température du bain-marie à 100° C. durant une heure, pour se débarrasser de l'acide bromhydrique. Par distillation dans le vide, on obtient l'acide α -bromo- δ -chlorovalérianique. Rendement: 80.1 g., 93%. P. é. 165° à 170° C. à 17 mm. Indice de réfraction: n_D^{20} 1.515. Calculé pour $C_5H_8O_2ClBr$: Cl, Br, 53.6%. Trouvé: Cl, Br, 52.0%.

Acide α,δ -dichlorovalérianique (X)

(a) Chloruration de l'acide δ -chlorovalérianique au moyen du chlore

On place 68.5 g. d'acide δ -chlorovalérianique en présence de 4.0 g. de trichlorure de phosphore, dans une grande éprouvette maintenue à une température de 150° C. au moyen d'un bain de cire. On fait barbotter le chlore gazeux au moyen d'un tube terminé par un disque de verre poreux. On peut suivre la marche de la réaction, qui dure environ cinq heures, en pesant périodiquement l'éprouvette ou en prenant l'indice de réfraction. On distille l'acide α,δ -dichlorovalérianique. Rendement: 71.1 g., 83.3%. P. é. 160° à 162° C. à 21 mm. Indice de réfraction: n_D^{20} 1.488. Calculé pour $C_5H_8O_2Cl_2$: Cl, 41.5%. Trouvé: Cl, 40.8%.

(b) Chloruration de l'acide δ -chlorovalérianique au moyen du chlorure de sulfuryle

Dans un ballon à large col, on place 27.3 g. d'acide δ -chlorovalérianique (0.2 mole) et 4 g. de trichlorure de phosphore. On active le mélange en l'éclairant pendant quelque temps au moyen d'une lampe à rayons ultra-violets. Puis, on laisse tomber lentement 150 ml. de chlorure de sulfuryle fraîchement distillé. On laisse alors reposer pour la nuit, et on chauffe le mélange à reflux sur un bain-marie bouillant pendant six heures. On enlève l'excès de chlorure de sulfuryle par évaporation sous pression réduite et on distille l'acide dichloré. Rendement: 24.6 g., 72.0%. P. é. 154° à 156° C. à 18 mm.

(c) Chloruration du δ -chlorovaléronitrile au moyen du chlorure de sulfuryle

Dans un ballon muni d'un tube réfrigérant et d'un entonnoir à décantation, on place 47.0 g. de δ -chlorovaléronitrile (0.4 mole), 5 g. de trichlorure de phosphore et une trace d'iode pulvérisé. On active le mélange en l'éclairant quelque temps au moyen d'une lampe à rayons ultra-violets. Puis on laisse tomber 100 ml. de chlorure de sulfuryle fraîchement distillé. On chauffe alors à reflux sur bain-marie pendant 15 h. On ajoute un mélange de 100 ml. d'acide chlorhydrique et de 40 ml. d'acide acétique glacial, et on fait bouillir à reflux pendant deux heures. Après avoir ajouté 200 ml. d'eau froide, on extrait trois fois à l'éther, et on sèche la solution éthérée sur du sulfate de sodium anhydre. Après avoir évaporé l'éther, on distille dans le vide. On obtient par fractionnement les acides δ -chlorovalérianique et α,δ -dichlorovalérianique.

Rendement en acide δ -chlorovalérianique: 14.4 g., 26.4%. P. é. 146° à 149° C. à 23 mm. Rendement en acide α,δ -dichlorovalérianique: 26.0 g., 38.0%. P. é. 155° à 160° C. à 22 mm.

Acide δ -hydroxyvalérianique (V)

(a) A partir du δ -chlorovaléronitrile

Dans un ballon muni d'un réfrigérant, on mélange 117.5 g. de δ -chlorovaléronitrile (1.0 mole), 200 g. d'hydroxyde de potassium, 660 ml. d'éthanol et 100 ml. d'eau distillée. On chauffe le ballon à reflux sur bain-marie pendant six heures. Après avoir refroidi le mélange, on neutralise par de l'acide chlorhydrique, jusqu'à légère coloration rose avec la phénolphthaléine. On porte alors le tout au froid pour la nuit; on filtre le mélange et on lave soigneusement les sels de potassium au moyen d'une solution alcoolique légèrement acide. On évapore les filtrats obtenus jusqu'à un volume d'environ 200 ml. En acidifiant avec un grand excès d'acide chlorhydrique concentré, on obtient deux couches de liquide. On extrait à l'éther, on sèche la solution étherée sur du sulfate de sodium anhydre et on distille l'éther sous pression réduite. Le résidu est une huile jaune, composée principalement d'acide δ -hydroxyvalérianique. Rendement brut: 100.3 g., 84.7%.

(b) A partir du dihydropyranne

On ajoute 380 ml. d'acide chlorhydrique 0.02 *N* à 34 g. de dihydropyranne (0.4 mole). On porte le mélange à l'ébullition, en ayant soin de bien agiter. La solution devient alors limpide. On continue l'ébullition pour une dizaine de minutes. A ce stage, le dihydropyranne est complètement hydrolysé en aldéhyde δ -hydroxyvalérianique. On refroidit la solution et on neutralise par une solution diluée d'hydroxyde de sodium, jusqu'à légère coloration rose à la phénolphthaléine. On ajoute 200 ml. de soude *N* et on introduit très lentement 42.0 g. de permanganate de potassium; pendant toute la durée de l'addition du permanganate, le mélange est agité vigoureusement. On laisse alors le tout à la température de la chambre pour la nuit. On acidifie et on extrait à l'éther au moyen d'un extracteur continu. Après 24 h., on distille l'éther et on obtient 30.7 g. d'une huile épaisse, composée principalement d'acide δ -hydroxyvalérianique. Le produit n'a pas été purifié, mais a aussitôt été transformé en acide δ -bromovalérianique.

Acide δ -bromovalérianique (VI)

On place dans un ballon muni d'un réfrigérant 49.2 g. d'acide δ -hydroxyvalérianique provenant soit du δ -chlorovaléronitrile, soit du dihydropyranne, 104 g. d'acide bromhydrique à 48% et 34.3 ml. d'acide sulfurique concentré. On chauffe le mélange sur un bain-marie bouillant, pendant cinq heures. On le verse dans 300 ml. d'eau froide et on l'extrait à l'éther. On sèche la solution étherée sur du sulfate de sodium anhydre, on évapore l'éther, et on distille dans le vide l'acide δ -bromovalérianique. Rendement: 40.0 g., 53%. P. f. 38°

à 39° C. Litt.: 38° à 39° C. (1).^{*} P.é. 152° C. à 17 mm. Litt.: 114° à 119° C. à 2 mm. (5). Calculé pour $C_8H_9O_2Br$: Br, 44.3%. Trouvé: Br, 42.8%.

Acide α,δ -dibromovalérianique (VII)

On traite 30.5 g. d'acide δ -bromovalérianique par 40.0 g. de brome, en présence de 2.0 g. de phosphore rouge, tel que décrit pour la préparation de l'acide α -bromo- δ -chlorovalérianique. On obtient ainsi l'acide α,δ -dibromovalérianique. Rendement: 38.4 g., 87.5%. P. é. 168° à 172° C. à 14 mm. Litt.: 171° à 174° C. à 13 mm. (1). Calculé pour $C_8H_8O_2Br_2$: Br, 61.5%. Trouvé: Br, 60.0%.

Acide α -chloro- δ -bromovalérianique (VIII)

On fait barbotter du chlore gazeux dans 84.0 g. d'acide δ -bromovalérianique, en présence de 4.0 g. de trichlorure de phosphore, suivant la méthode décrite pour l'acide α,δ -dichlorovalérianique. Par distillation dans le vide, on obtient l'acide α -chloro- δ -bromovalérianique. Rendement: 82.0 g., 82.0%. P. é. 170° à 175° C. à 21 mm. Indice de réfraction: n_D^{20} 1.515. Calculé pour $C_8H_8O_2ClBr$: Cl, Br, 53.6%. Trouvé: Cl, Br, 53.9%.

DL-proline (XI)

On mélange 0.05 mole d'un acide valérianique α,δ -dihalogéné et 150 ml. d'ammoniaque concentrée, dans un petit ballon à pression, qu'on place à l'étuve à 70° C. pendant 48 h. On évapore alors le mélange à sec, sous pression réduite. On dissout le résidu solide dans l'eau et on agite pendant une heure avec de l'hydroxyde d'argent, fraîchement précipité à partir de 17.0 g. de nitrate d'argent et de 4.0 g. d'hydroxyde de sodium. On filtre, on lave soigneusement à l'eau chaude le précipité d'halogénure d'argent et on sature les filtrats combinés d'hydrogène sulfuré. On filtre à nouveau et on chasse l'excès d'hydrogène sulfuré du filtrat, par ébullition prolongée. Après traitement au noir animal, on obtient la solution de proline débarrassée des sels inorganiques.

On transforme la proline à l'état de sel de cuivre en faisant bouillir la solution ainsi obtenue avec un précipité d'hydroxyde cuivrique provenant de 16.0 g. de sulfate de cuivre et de 11.2 g. d'hydroxyde de potassium. Après avoir filtré l'hydroxyde cuivrique non transformé, on évapore à sec sous pression réduite, on dissout le résidu dans 25 ml. d'eau chaude, et on porte la solution violette au froid. Après cristallisation, on filtre le prolinat de cuivre pratiquement pur et on ajoute un égal volume d'alcool éthylique, ce qui a pour effet de précipiter les dernières traces de prolinat de cuivre, mais aussi d'entraîner des quantités appréciables de sels de cuivre des résidus. Cette deuxième fraction doit d'abord être recristallisée avant de pouvoir être ajoutée à la

^{*} Les points de fusion ne sont pas corrigés.

fraction principale. Le prolinat de cuivre est obtenu sous forme de cristaux bleus, qui par chauffage à l'étuve à 100° C. pendant quelques heures perdent leur molécule d'eau de cristallisation, et prennent une couleur violette caractéristique. Calculé pour $C_{10}H_{16}O_4N_2Cu$: N, 9.62%. Trouvé: N, 9.66%.

On procède exactement de la même façon pour cycliser les acides α -bromo- δ -chlorovalérianique, α,δ -dibromovalérianique, α,δ -dichlorovalérianique et α -chloro- δ -bromovalérianique.

Pour les cyclisations effectuées à des températures supérieures à 70° C. on se sert d'un autoclave. La technique pour l'isolement de la proline reste cependant la même.

Il est aussi possible d'isoler la proline sans qu'il soit nécessaire d'éliminer les sels d'ammonium sous forme de sels d'argent ou même de sels de plomb. On évapore à sec les produits d'amination, on assèche les résidus en les lavant deux ou trois fois dans l'acétone, on les place dans la capsule d'un extracteur Soxhlet et on extrait la DL-proline par l'alcool éthylique absolu. Une certaine quantité du bromure d'ammonium s'y dissout, mais le chlorure d'ammonium demeure insoluble. Après environ une heure d'extraction, on évapore la solution alcoolique. Le résidu est alors traité par l'hydroxyde cuivrique, tel que décrit plus haut. La faible quantité de bromure d'ammonium qui s'est dissoute dans l'alcool n'interfère pas dans l'isolement du prolinat de cuivre. Nous avons ainsi obtenu des rendements qui se comparent favorablement à ceux obtenus par la technique des sels d'argent.

On peut aussi faire réagir directement la proline avec l'hydroxyde de cuivre, sans éliminer les sels d'ammonium. Dans ce cas cependant, le rendement est légèrement inférieur, à cause de la difficulté de séparer la dernière fraction de prolinat de cuivre de la solution concentrée des sels ammoniacaux.

Picrate de proline

On fait passer de l'hydrogène sulfuré dans une solution contenant 2.0 g. de prolinat de cuivre. Après avoir filtré le précipité de sulfure de cuivre, on chasse l'hydrogène sulfuré par ébullition. On ajoute alors 4.0 g. d'acide picrique et on chauffe la solution à reflux pendant une heure. Par refroidissement, on obtient des cristaux jaunes, qui après lavage à l'éther, et recristallisation dans l'eau, donnent de fines aiguilles, fondant à 135° à 137° C. Litt. 135° à 137° C. (2). Rendement: 4.0 g., 90%.

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THE SYNTHESIS OF SOME PYRIDOCARBAZOLES¹

BY RICHARD H. F. MANSKE AND MARSHALL KULKA

Abstract

Three new pyridocarbazoles, namely, 11-pyrido(4,3-*a*)-, 11-pyrido(3,4-*a*)-, and 10-pyrido(3,4-*b*)- or 9-pyrido(4,3-*c*)-carbazole have been synthesized from the hydrazones of cyclohexanone and 5-, 8-, and 7-hydrazinoisoquinoline respectively by ring closure and dehydrogenation of the resulting tetrahydropyridocarbazoles. In unsuccessful attempts to determine which of the two possible pyridocarbazoles is formed from the hydrazone of cyclohexanone and 7-hydrazinoisoquinoline, 11-methyl-10-pyrido(3,4-*b*)carbazole was also synthesized. The hydrazone of cyclohexanone and 7-amino-8-chloroisoquinoline failed to undergo ring closure.

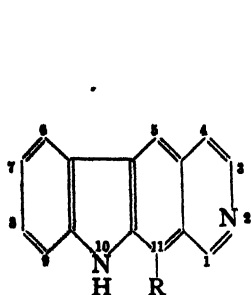
The fusion of the isoquinoline ring to the 2,3-position of indole or the fusion of a pyridine ring to carbazole may result in six isomeric pyridocarbazoles, namely, 10-pyrido(3,4-*b*)- (I), 9-pyrido(4,3-*c*)- (II), 11-pyrido(4,3-*a*)- (III), 11-pyrido(3,4-*a*)- (IV), 10-pyrido(4,3-*b*)- (V), and 9-pyrido(3,4-*c*)- (VI) carbazoles. There does not seem to be a description of any of these complex ring systems in the literature. Success did not attend attempts to fuse a pyridine ring onto carbazole by cyclization of N-formyl-, N-carbethoxy-, and N-acetyl-β-(5,6,7,8-tetrahydro-3-carbazolyl)ethylamine to I (3). It was therefore decided to attempt to synthesize I and its isomers by fusing an indole ring onto isoquinoline. The general method adopted was the Fischer indole ring closure of the hydrazone (VII) of cyclohexanone and the appropriate hydrazinoisoquinoline, followed by dehydrogenation of the resulting tetrahydropyridocarbazole. The hydrazone of cyclohexanone and 5-hydrazinoisoquinoline (4) when treated with 17% sulphuric acid at room temperature or by warming underwent ring closure almost quantitatively to give 7,8,9,10-tetrahydro-11-pyrido(4,3-*a*)carbazole. Dehydrogenation of this to III required heating with platinum at 360° C. for five hours in an atmosphere of nitrogen. The pyridocarbazole IV was prepared similarly by cyclizing the hydrazone of cyclohexanone and 8-hydrazino-5-chloroisoquinoline (4) and dechlorinating and dehydrogenating the resulting 5-chloro-7,8,9,10-tetrahydropyrido(3,4-*a*)carbazole.

Theoretically the hydrazone of cyclohexanone and 7-hydrazinoisoquinoline (4) can undergo the Fischer indole ring closure in two ways to produce 6,7,8,9-tetrahydro-10-pyrido(3,4-*b*)carbazole and 5,6,7,8-tetrahydro-9-pyrido(4,3-*c*)carbazole, these being hydro derivatives of I and II. However, it was found that only one of these is formed. In an attempt to determine the structure of this pyridocarbazole, the hydrazone of cyclohexanone and 7-hydrazino-8-chloroisoquinoline (4) was treated with 17% sulphuric acid and with dry

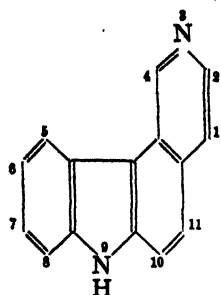
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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

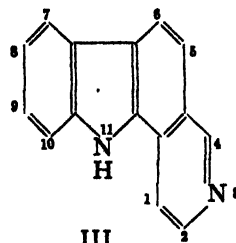
hydrogen chloride in organic solvents but no 11-chloro-6,7,8,9-tetrahydro-10-pyrido(3,4-*b*)carbazole could be obtained. Instead, a small amount of an unidentified chlorine-free compound was obtained when cyclization was carried



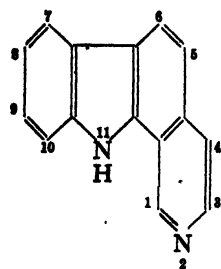
I (R=H)
VIII (R=CH₃)



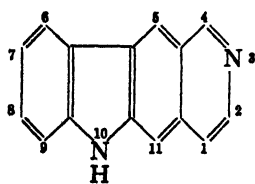
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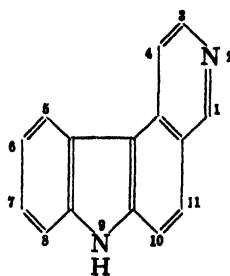
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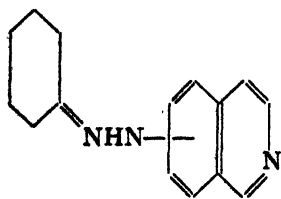
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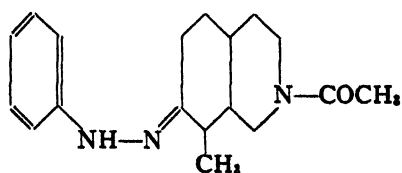
V



VI



VII



IX

out at 100° C. or higher, and low-boiling decomposition products, one of which was 8-chloroisoquinoline (2), resulted when cyclization was attempted at room temperature over an extended period of time. The same pyridocarbazole (I or II) was obtained from the phenylhydrazone of N-acetyl-7-ketodecahydroisoquinoline by ring closure followed by deacetylation and dehydrogenation.

In another attempt to determine whether the pyridocarbazole is the linear, I or angular compound II, 11-methyl-10-pyrido(3,4-*b*)-carbazole (VIII) was synthesized by ring closure of the phenylhydrazone of *cis*- and *trans*-N-acetyl-7-keto-8-methyldecahydroisoquinoline (IX) (6) followed by deacetylation and dehydrogenation. However, VIII could not be demethylated via oxidation and decarboxylation. Oxidation of VIII with selenium dioxide or chromyl chloride resulted in resinous inorganic material. This is not surprising in view of the behavior of carbazole (1, 5) and 1-methylcarbazole to various oxidizing agents. Further work on the structure determination of I and II and the synthesis of V and VI is in progress.

Experimental

The Hydrazone of Cyclohexanone and 5-Hydrazinoisoquinoline

To a hot solution of 5-hydrazinoisoquinoline (4) (7.8 gm.) in methanol (60 cc.) was added cyclohexanone (5.0 gm.) and the solution heated under reflux for one-half hour. The solvent was distilled off under reduced pressure and the solid residue crystallized from benzene or ethyl acetate; light-yellow prisms, m.p. 129° to 131° C.;* yield, 8.7 gm. or 74%. Calc. for $C_{15}H_{17}N_3$: C, 75.29; H, 7.15; N, 17.55%. Found: C, 75.45, 75.45; H, 6.95, 7.06; N, 16.97, 16.99%.

*7,8,9,10-Tetrahydro-11-pyrido(4,3-*a*)carbazole*

A solution of the hydrazone of 5-hydrazinoisoquinoline (8.5 gm.) in 17% sulphuric acid (by weight) (100 cc.) was allowed to stand at room temperature for 15 hr. The reaction mixture, which contained the yellow precipitated sulphuric acid salt, was then heated on the steam bath for one hour in order to complete the reaction, cooled, filtered, and washed with water. The sulphate (m.p. 247° to 250° C.) (8.5 gm.) was dissolved in boiling water (1500 cc.) and the solution basified with sodium hydroxide and cooled. The white precipitate was filtered, washed, and dried, yield 5.9 gm. or 72%; m.p. 218° to 219° C. Crystallization from acetone gave white needles (5.5 gm. from three crops); m.p. 219 to 220° C. Calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61%. Found: C, 80.83, 81.14; H, 6.38, 6.53; N, 12.00, 11.90%.

*11-Pyrido(4,3-*a*)carbazole (III)*

7, 8, 9, 10-Tetrahydro-11-pyrido(4,3-*a*)carbazole (1.0 gm.) was mixed with platinum black (Adams catalyst) (0.50 gm.) and then heated in an atmosphere of nitrogen at 360° C. for five hours. It was then sublimed at 50 μ pressure and a temperature of about 230° C. The sublimate (0.70 gm.) was crystallized from methanol, yielding white needles; m.p. 256 to 257° C. Calc. for $C_{15}H_{10}N_2$: C, 82.51; H, 4.63; N, 12.83%. Found: C, 82.20, 82.17; H, 5.12, 4.87; N, 12.66%.

* All melting points are corrected.

Hydrazone of Cyclohexanone and 5-Chloro-8-hydrazinoisoquinoline (4)

This hydrazone was prepared in a manner similar to that of 5-hydrazinoisoquinoline above, light-yellow needles; m.p. 144 to 147° C. (with decomposition) after crystallization from methanol. Calc. for $C_{15}H_{16}N_2Cl$: C, 65.82; H, 5.85; N, 15.36%. Found: C, 66.02, 65.72; H, 6.02, 5.98; N, 15.62%.

5-Chloro-7,8,9,10-tetrahydro-11-pyrido(3,4-a)carbazole

A solution of the crude hydrazone of cyclohexanone and 5-chloro-8-hydrazinoisoquinoline (1.6 gm.) in 17% sulphuric acid (75 cc.) was allowed to stand at room temperature overnight and then heated on the steam bath for one hour. The yellow sulphuric acid salt was filtered, dissolved in a boiling solution of water (400 cc.) and ethanol (400 cc.), and basified with sodium hydroxide. The ethanol was distilled off under reduced pressure and the aqueous suspension filtered; yield of light-yellow solid, 1.2 gm. or 80%; crystallized from acetone and methanol, light-yellow needles, m.p. 323° to 324° C. Calc. for $C_{15}H_{13}N_2Cl$: C, 70.18; H, 5.07; N, 10.91%. Found: C, 70.05, 70.37; H, 5.26, 5.20; N, 10.79%.

11-Pyrido(3,4-a)carbazole(IV)

To tetralin (100 cc.) was added platinum catalyst (0.3 gm.) and 5-chloro-7,8,9,10-tetrahydro-11-pyrido(3,4-a)carbazole (0.5 gm.) and the reaction mixture heated under reflux until no more hydrogen chloride was evolved (40 hr.) as indicated by bubbling the nitrogen swept gas into silver nitrate solution. The tetralin was removed under reduced pressure, more platinum catalyst (0.1 gm.) was added to the residue, and the mixture heated at 330° C. for four hours in an atmosphere of nitrogen, in order to complete the dehydrogenation. The product was then sublimed at ca. 220° C. (1 mm.), yielding 0.24 gm. or 56% of yellow sublimate; crystallized from methanol, light-yellow prisms, m.p. 280° to 282° C. Calc. for $C_{15}H_{10}N_2$: C, 82.51; H, 4.63; N, 12.83%. Found: C, 82.49, 82.30; H, 5.16, 4.94; N, 12.80%.

Hydrazone of Cyclohexanone and 7-Hydrazinoisoquinoline (4)

This hydrazone was prepared in a manner similar to that of 5-hydrazinoisoquinoline above; m.p. 137° to 140° C. from benzene and from ethyl acetate. Calc. for $C_{15}H_{17}N_2$: C, 75.29; H, 7.15%. Found: C, 74.93, 74.80; H, 7.24, 7.28%.

6,7,8,9-Tetrahydro-10-pyrido(3,4-b)carbazole or 5,6,7,8-Tetrahydro-9-pyrido-(4,3-c)carbazole

A solution of the hydrazone of cyclohexanone and 7-hydrazinoisoquinoline (crude, prepared from 0.90 gm. of 7-hydrazinoisoquinoline) in 17% sulphuric acid was allowed to stand at room temperature overnight and then heated on the steam bath for one-half hour. The cooled solution was basified with sodium hydroxide and the precipitated tarry material extracted with ether. The ether was distilled off and the residue sublimed at ca. 220° C. (50 μ).

The sublimate (0.5 gm. or 40%) was crystallized from acetone or methanol; yellow prisms, m.p. 227° to 228° C. Calc. for $C_{15}H_{14}N_2$: C, 81.04; H, 6.34; N, 12.61%. Found: C, 81.21, 81.03; H, 6.48, 6.45; N, 12.79, 13.00%.

10-Pyrido(3,4-b)carbazole (I) or 9-Pyrido(4,3-c)carbazole (II)

(a) The tetrahydro derivative of I or II (0.5 gm.) was mixed with platinum catalyst (0.1 gm.) and heated at 330° C. for seven hours in an atmosphere of nitrogen and then sublimed at *ca.* 250° C. (2 mm.). The sublimate (0.47 gm.) was crystallized from methanol; light-yellow needles, m.p. 249° to 250° C. Calc. for $C_{15}H_{10}N_2$: C, 82.51; H, 4.63; N, 12.83%. Found: C, 82.27, 82.52; H, 4.67, 5.22; N, 12.66%.

(b) 7-Hydroxyisoquinoline was hydrogenated and acetylated in the same manner as was 7-hydroxy-8-methylisoquinoline (6) to yield *N*-acetyl-7-hydroxy-1,2,3,4-tetrahydroisoquinoline; m.p. 155° to 158° C., from methanol. Calc. for $C_{11}H_{13}O_2N$: C, 69.11; H, 6.80; N, 7.33%. Found: C, 68.97, 69.09; H, 6.80, 6.67; N, 7.19, 7.13%. This was then further hydrogenated (6) and the crude *N*-acetyl-7-hydroxydecahydroisoquinoline without isolation oxidized to *N*-acetyl-7-ketodecahydroisoquinoline (6); yield, 30%. The latter was a colorless liquid boiling at about 200° C. (2 mm.). The oily phenylhydrazone from this, which was prepared in the same way as was IX (see below), was ring closed and deacetylated by heating under reflux in 6 *N* hydrochloric acid for two hours. The resulting crude octahydro derivative(s) of I or II (0.2 gm.) was dehydrogenated by heating with platinum oxide at 250° C. for three hours in an atmosphere of nitrogen. The product consisted of resinous material for the greater part, a low-boiling fraction which was not investigated, and a yellow solid (0.01 gm.) which sublimed at 200° to 220° C. (1 mm.) and melted at 245° to 247° C. alone or in admixture with the I or II obtained in (a).

Phenylhydrazone of cis-N-Acetyldecahydro-7-keto-8-methylisoquinoline (IX)

A solution of *cis*-*N*-acetyldecahydro-7-keto-8-methylisoquinoline hydrate (6) (1 gm.), methanol (10 cc.), and phenylhydrazine (1 gm.) was heated under reflux for one-half hour. The cooled reaction mixture was filtered and the white hydrazone (1.1 gm. or 83%) was crystallized from methanol; white prisms, m.p. 190° to 198° C. Calc. for $C_{18}H_{26}N_3O$: C, 72.19; H, 8.42; N, 14.04%. Found: C, 72.12, 72.02; H, 8.38, 8.30; N, 13.83, 14.12%.

N-Acetyl-1,2,3,4,5,11,12,13-octahydro-11-methyl-10-pyrido(3,4-b)carbazole

The phenylhydrazone of *N*-acetyldecahydro-7-keto-8-methylisoquinoline (IX) (1.1 gm.) was added to 17% sulphuric acid (50 cc.) and the reaction mixture heated at 70° to 80° C. for one-quarter hour. The white precipitate which appeared soon after the hydrazone had dissolved was filtered from the cooled reaction mixture, washed with water and dried; yield 0.15 gm., m.p. 235° to 237° C. Crystallization from ethanol yielded white needles; m.p. 238° to 239° C. Calc. for $C_{18}H_{22}N_2O$: C, 76.56; H, 7.87; N, 9.92%. Found: C, 76.40, 76.69; H, 7.89, 7.97; N, 10.10, 10.27%.

11-Methyl-10-pyrido(3,4-*b*)carbazole (VIII)

(a) N-Acetyl-1,2,3,4,5,11,12,13-octahydro-11-methyl-10-pyrido(3,4-*b*)carbazole (0.1 gm.) was added to 6 *N* hydrochloric acid (10 cc.) and the reaction mixture heated under reflux for three hours. The resulting solution was taken to dryness under reduced pressure, the residue dissolved in water, and the solution basified with sodium hydroxide. The semisolid precipitate was filtered off and heated with platinum oxide catalyst (0.05 gm.) in an atmosphere of nitrogen at 230° to 240° C. for three hours. Sublimation at *ca.* 240° C. (2 mm.) yielded 7 mgm. of solid which crystallized from acetone as intensely yellow needles; m.p. 284° to 286°C.

(b) The hydrazone IX (0.2 gm.) was added to 6 *N* hydrochloric acid (10 cc.) and the reaction mixture heated under reflux for two hours. The solution was basified with sodium hydroxide, and the gummy precipitate filtered and dehydrogenated as in (a); yield of sublimate was 0.047 gm. or 30% which when crystallized from acetone melted at 284° to 286° C. Calc. for $C_{16}H_{12}N_2$: C, 82.71; H, 5.21; N, 12.06%. Found: C, 82.94, 82.81; H, 5.20, 5.30; N, 11.88, 12.32%.

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THE MECHANISM OF SULPHATE ATTACK ON PORTLAND CEMENT¹

BY F. M. LEA

Abstract

Tests on the expansion of mortars in sulphate solutions indicate that the conversion of calcium hydroxide to gypsum is a contributory factor. The increased resistance to attack obtained by curing in steam under pressure appears primarily to be due to the suppression of this reaction and to the decreased permeability of the mortar.

It seemed appropriate that a paper contributed to the present number in honor of Professor Thorvaldson should deal with a subject to which he has made major contributions. The opportunity has, therefore, been taken to present some results of work carried out intermittently before the war which, though incomplete, throw some further light on the mechanism of sulphate attack on Portland cement.

The action of sulphate solutions on Portland cement is determined by the nature of the chemical reaction and by physical factors such as the permeability of the mortar or concrete concerned and the degree to which the more reactive constituents of the set cement may be protected by surface films of less reactive components. The chemical reactions possible are (i) the conversion of calcium hydroxide in the set cement to calcium sulphate, (ii) the conversion of hydrated calcium aluminates and ferrites to calcium sulphoaluminate or sulphoferrite or their solid solutions, and (iii) the decomposition of hydrated calcium silicates. In calcium sulphate solution only (ii) can occur, but in sodium sulphate solution (i) may occur in addition. The reaction



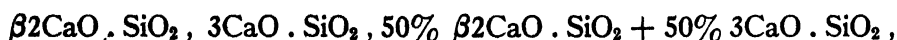
proceeds to a considerable extent from left to right. Thus, from the data of Hansen and Pressler (6), if a solution containing 53.2 gm. per liter sodium sulphate is brought into contact with excess solid calcium hydroxide and calcium sulphate, about 30% of the SO_3 is deposited out as calcium sulphate by reaction with the calcium hydroxide before equilibrium is reached. With a sodium sulphate solution of 20.6 gm. per liter about 20% of the SO_3 is deposited as calcium sulphate. Under conditions where the supply of sodium sulphate is maintained the extent of conversion will increase, but its rate will be determined by the speed with which sulphate ions can diffuse in and hydroxyl ions out of the mortar or concrete. In practice, therefore, with dense mortars or concretes, only partial conversion of calcium hydroxide to calcium sulphate may occur even over long periods. The solid volume more than doubles during the conversion, the respective molecular volumes of Ca(OH)_2 and

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$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ being 33.2 and 74.3 cc. With magnesium sulphate all three reactions can proceed, since the pH value of saturated magnesium hydroxide (about 10.5) is below that necessary to stabilize the hydrated calcium silicates. In addition, calcium sulphoaluminate is itself unstable at a pH of 10.5 and, though first formed, eventually decomposes again to form gypsum and hydrated alumina.

Thorvaldson (11) and his collaborators have compared the rates of expansion in sulphate solutions of mortar bars containing pure cement compounds as cementing agents. In magnesium sulphate solutions decreasing rates of expansion of 1 : 10 mortars were found in the order



while with sodium and calcium sulphate solutions the expansions were very small in all cases, even though microscopic examination showed the presence of gypsum crystals in the mortar. The substitution of 20% $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ for the silicates led to much increased rates of expansion in all sulphate solutions and the mixes with $3\text{CaO} \cdot \text{SiO}_2$ expanded more rapidly than those with $\beta 2\text{CaO} \cdot \text{SiO}_2$, in contrast to the relative behavior of these two compounds when used alone. In later tests on denser mortars prepared from laboratory-made cement, Bogue, Lerch, and Taylor (3) found the resistance to attack by sulphate solutions increased somewhat as the content of $3\text{CaO} \cdot \text{SiO}_2$ was raised at the expense of $2\text{CaO} \cdot \text{SiO}_2$, though the effect was pronounced only with cements of relatively high $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ contents. They attributed this to improvements in water-tightness and strength rather than to any inherent higher resistance to sulphate attack of $3\text{CaO} \cdot \text{SiO}_2$ compared with $2\text{CaO} \cdot \text{SiO}_2$. The available evidence does not, therefore, indicate clearly the influence on the expansion of the conversion to gypsum of the calcium hydroxide liberated during the hydration of $3\text{CaO} \cdot \text{SiO}_2$. Some tests were carried out in the present work to obtain more definite evidence.

It has also long been known (9) that the resistance of Portland cement products to attack by sulphate solutions is much increased by curing in high pressure steam which causes changes in the hydrated cement products and at the same time decreases the permeability of the mortar or concrete. Apart from the formation of a crystalline hydrated dicalcium silicate (9) from both $3\text{CaO} \cdot \text{SiO}_2$ and $\beta 2\text{CaO} \cdot \text{SiO}_2$, a major change is in the form of the alumina and iron compounds. Flint, McMurdie, and Wells (4) have shown that, in high pressure steam, hydrated tricalcium aluminate and the corresponding ferrite are converted into hydrogarnets consisting of a solid solution of the general formula



These hydrogarnets proved very resistant to the action of sodium sulphate solutions containing sufficient calcium hydroxide to prevent hydrolysis (5), but the resistance to magnesium sulphate solution may not be as high since the pH of saturated magnesium hydroxide solution may be too low to stop hydrolysis. A further important change with silica sands is their reaction

with the free calcium hydroxide to form hydrated calcium silicates. The substitution of a limestone sand for silica enables the latter effect to be eliminated. There is also evidence (7, 8) that high pressure steam treatment of calcium carbonate leads to some reaction which tends to cause expansion, and so prevent the normal decrease in permeability of the mortar. Some tests were, therefore, made to examine the effect of substitution of a limestone for sand as aggregate.

Experimental

Measurements were made of the expansion of cylindrical mortar rods 5 in. long and 1 in. diameter. The mortars varied considerably in composition, but the consistence of the mix, which was a dry type, was standardized and similar to that used for making mortar briquettes for tensile test in the British Standard for Portland cement (BS 12). The rods were compacted in a standard manner and cured, except where otherwise stated, for one day in moist air and six days in water at 18° C. before immersion in solutions of 5% (anhydrous) sodium or magnesium sulphate at 18° C. Stainless steel balls cast in the ends of the rods served as reference points for measurement of changes in length. All results are the mean of measurements on four rods.

Results

The first series of tests were made on mortars containing only lime and silica, which were cured either in water or high pressure steam and in which the composition was so adjusted as to leave varying contents of free calcium hydroxide. The mixes were as follows, by weight:—

No.	CaO	SiO ₂ (as silica gel)	120 B.S. mesh sand	18-25 B.S. mesh sand
I	1	0.33	1.62	4.55
II	1	0.555	1.805	5.5
III	1	—	2.36	5.5
IV	1	—	3.75	8.75

The ratio of total sand content to cementing agent, and of coarse sand to fine sand and silica gel, were maintained constant as shown below, in order to keep the various mixes as similar physically as possible.

Ratio for various mixes	I	II	III	IV
$\frac{\text{Total SiO}_2}{\text{CaO}}$	6.5	7.8	7.8	12.5
$\frac{\text{Total sand}}{\text{CaO} + \text{SiO}_2 \text{ (as gel)}}$	4.7	4.7	—	—
$\frac{\text{Coarse sand}}{\text{SiO}_2 \text{ (as gel)} + \text{fine sand}}$	2.33	2.33	2.33	2.33

The silica gel used contained about 80% SiO_2 and the lime was a commercial hydrate containing about 95% Ca(OH)_2 . The weight proportions given above are based on the anhydrous constituents.

The expansions observed in sulphate solutions, and other relevant data, are shown in Table I.

TABLE I

No.	Type mix	Curing	% free CaO after curing	Storage solution	Weeks' storage	% expansion
I	Lime : silica gel : sand	6 weeks moist air, followed by 17 weeks in water, 18° C.	4	Na_2SO_4	200	0.20
				MgSO_4	90	0.19
II	Lime : silica gel : sand	6 weeks moist air, followed by 34 weeks in water, 18° C.	0	Na_2SO_4	120	Zero
				MgSO_4	90	0.02
					120	0.43
III	Lime : sand	Autoclaved 7 hours, 183.5° C.	4.3	Na_2SO_4	90	0.04
					150	0.06
				MgSO_4	90	0.14
					150	0.28
IV	Lime : sand	Autoclaved 7 hours, 183.5° C.	0.8	Na_2SO_4	150	Zero
				MgSO_4	90	0.04
					150	0.13

The free lime values were determined by extraction of 1 gm. with 200 cc. of a solution containing 0.06 gm. CaO per 100 cc. by the method described by Bakewell and Bessey (1). Hydrolysis of hydrated calcium monosilicate is avoided by this procedure, but the values obtained can be regarded only as very approximate. Very similar values were obtained on extraction with a solution containing 0.02 gm. CaO per 100 cc.

Further tests, shown in Table II, were designed to show the effect of removal of free lime from a Portland cement mortar by carbonation.

It is evident from a comparison (Table I) of Mix I with II, or III with IV, that a calcium silicate bonding agent is not attacked by sodium sulphate solutions, as earlier work of Thorvaldson has shown, but that the conversion of any free Ca(OH)_2 present to $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ leads to an expansion. A somewhat similar comparison is provided by V and VI (Table II) but in this case, with Portland cement as the binding agent, the removal of free calcium hydroxide by carbonation only retards expansion in sodium sulphate solutions, since formation of calcium sulphotoaluminate from the alumina compounds of the set cement can still occur. The protective effect of carbonate films may also have had an influence in retarding the expansion, making the evidence less definite. In magnesium sulphate solution the calcium silicate binding agent of Mixes I-IV is attacked, but the expansion is accelerated by the presence of free Ca(OH)_2 in the mortar. Similar results are seen from V and VI, where the presence of alumina compounds in the set cement leads to more rapid expansion.

TABLE II

Ref. No.	Mix proportions by weight	Curing	% free CaO after curing	% CO ₂ after curing	Storage solution	Weeks' storage	% expansion
V	1 Portland Cement A 1 Ground sand* 6 18-25 mesh sand	28 days in carbon dioxide at 50% R.H.	0.15	2.22	Na ₂ SO ₄	8	0.02
						20	0.18
					MgSO ₄	8	0.10
						20	0.60
VI	1 Portland Cement A 1 Ground sand* 6 18-25 mesh sand	28 days in CO ₂ -free air at 50% R.H.	1.90	0.20	Na ₂ SO ₄	8	0.40
					MgSO ₄	8	0.50

* Through 170 B.S. mesh.

Earlier tests (10) by Thorvaldson, Vigfusson, and Wolochow on a silica gel-lime mortar cured at normal temperature and containing 0.5% free CaO showed a high resistance to sodium sulphate solution but much less to magnesium sulphate, in general agreement with the results recorded here on Mix II.

The effect of high pressure steam treatment on the sulphate resistance of mortars with limestone and silica sands respectively is shown in Table III.

TABLE III

Ref. No.	Mix proportions by weight	Curing	Storage solution	Weeks' storage	% expansion
VII	1 Portland Cement A 1 Ground sand* 6 18-25 mesh sand	7 days water, 18° C.	Na ₂ SO ₄	8	0.24
			MgSO ₄	8	0.49
VIII	1 Portland Cement A 1 Ground sand* 6 18-25 mesh sand	Autoclaved 7 hours, 183.5° C.	Na ₂ SO ₄	200	Zero
			MgSO ₄	200	Zero
IX	1 Portland Cement A 1 Ground limestone* 6 18-25 mesh limestone	Autoclaved 7 hours, 183.5° C.	Na ₂ SO ₄	8	0.01
				20	0.28
			MgSO ₄	8	0.04
				20	0.52

* Through 170 B.S. mesh.

With a calcium carbonate sand the treatment increases the resistance to attack compared with a corresponding silica sand mortar cured at 18° C., but expansion is nevertheless still fairly rapid. In contrast, the silica sand mortar, after steam curing, remained immune from attack for nearly four years, when measurements were discontinued. It would appear, therefore, that the major cause of increase in the sulphate resistance of silica sand mortars on curing in high pressure steam is to be found in the suppression of the

reaction $\text{Ca(OH)}_2 \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, because of the removal of the free calcium hydroxide, or in the greater impermeability of the mass. The latter may be the result of a gross decrease in permeability or of the formation of protective films of the calcium hydroxide-sand reaction product over the cementing material. Bessey (2) has shown that in sand-lime brick manufacture the compounds formed are a mixture of hydrated monocalcium silicate and more basic silicates. These are not inert to attack by magnesium sulphate solution, but, being on the average less basic than the hydrated dicalcium silicate formed in the steam curing of Portland cement, they will be less reactive. The formation of hydrogarnets of higher sulphate resistance than hydrated tricalcium aluminate will also be a contributory factor in the increase of sulphate resistance, but not from the present evidence the major factor.

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THE INTERACTION OF METHANE AND METHANE- d_4 ON NICKEL AND THE STATE OF THE CATALYST SURFACE¹

BY MAURICE M. WRIGHT AND HUGH S. TAYLOR

Abstract

The interaction of methane and methane- d_4 on nickel has been re-examined. The data strengthen the previous concept of a dissociative adsorption of methane on the catalyst. The kinetic data indicate first-order disappearance of methane- d_4 with an activation energy of 20.9 kcal. between 100° and 255° C. Poisoning by carbonaceous residues occurs at all temperatures. First-order kinetics are indicated for the formation of methane- d_3 and methane- d_2 on the catalyst surface. Reaction of hydrogen with surface residues, after an exchange reaction, indicate that CX, CX₂, and CX₃ fragments are present on the surface where X is H or D. Higher temperatures favor an equilibrium between these fragments on the surface, equilibrium being displaced towards CX₃ as temperature increases. This equilibrium will be dependent on the heats of adsorption of the fragments and of hydrogen on the surface and therefore involves also the metal used as catalyst. The data suggest a basic approach to the mechanism of the Fischer-Tropsch synthesis on metal catalysts.

The interaction of methane with methane- d_4 on catalytic surfaces was first studied by Morikawa, Benedict, and Taylor (3) by means of infrared measurements. The rate-determining step was ascribed to activation of the carbon-hydrogen bond in each reactant by a process of dissociative adsorption on the surface, the first stage of which would be the formation of adsorbed methyl and adsorbed atomic hydrogen. In the limit, this dissociative process would yield adsorbed carbon and hydrogen atoms.

In the present work the exchange reaction has been measured with the aid of the mass spectrometer in order to seek more detail as to mechanism. A nickel - chromium oxide catalyst was used and the kinetics examined between 100° and 260° C. It was observed that the surface was partially poisoned for exchange by deposition of carbonaceous material, the nature of which has been studied by means of its interaction with hydrogen, since the surface poison could be removed and activity restored by such treatment. These studies have revealed definite evidence for the existence on the catalyst surface of the fragments CH₃, CH₂, CH, C, CD, CD₂, and CD₃. The dependence of their relative concentrations on temperature has been examined.

The results to be presented are preliminary to a final report (6). They indicate that, in the case of hydrocarbons, the dissociative mechanism is operative. The results in their bearing on the Fischer-Tropsch mechanism will also be indicated.

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Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, N.J., U.S.A.

The record of research by a younger generation of Canadian chemists constitutes a fitting tribute to the services rendered to chemical science by an older generation. This report on research carried through by one (M.M.W.) of a group of Canadian graduate students presently in residence in Princeton University, working under my direction, is offered in tribute to the services rendered by Prof. T. Thorvaldson of the University of Saskatchewan over a period of forty years. H.S.T.

Experimental

The exchange reaction was conducted in a static system and followed with the mass spectrometer by measuring the mass ratios 20/40, 19/40, and 18/40, the reference mass, 40, being argon. This gas, in 3% concentration, permitted measurement of the change in concentration of the deuterated methanes. Two other possible references, (a) the pressure behind the capillary leak of the spectrometer and (b) the mass, 12, or carbon peak, are less satisfactory, the pressure reference because of the small samples used and the consequent pressure change during analysis, the carbon peak because of its smallness, 1.2% of CD_4^+ and 1.8% of CH_4^+ . In the course of an experiment eight samples each approximately 0.5 cc. volume were removed, for the analyses, from an initial reaction mixture of about 40 cc.

Removal of carbonaceous residues from the catalyst surface was also followed by means of the mass spectrometer. The methane reaction mixture was removed and the catalyst evacuated at the temperature of the exchange reaction. Periods of evacuation from 30 min. to several hours were employed. Hydrogen to an amount of 30 cc. was then introduced, and 1.5 cc. samples were taken for analysis at intervals. In this case the hydrogen, mass 2, peak, corrected for methane formed, was the reference.

Between successive exchange reactions, according to Procedure B, the catalyst was treated with 30 cc. of pure hydrogen at 400° to 420° C. for two to four hours, and then evacuated at 400° C. for 1 to 20 hr. By this treatment removal of carbonaceous material was completed, each experiment beginning with the catalyst in substantially the same condition. In Procedure A, which was preliminary and exploratory, there were variations in the treatment between successive runs. These varying treatments yielded interesting divergencies from the results by Procedure B.

Preparation of Gases

Methane- d_4 was prepared by reacting pure deuterium oxide with aluminum carbide at room temperature in an evacuated apparatus. The carbide was dried by evacuation for several hours prior to reaction. The reaction is slow, and, according to Urey and Price (5), slower than with ordinary water. It was found, in our experiments, to be simpler to allow reaction to proceed at room temperature for about two days to form 2 liters of gas than to raise the pressure with another gas such as carbon dioxide and work at higher temperatures. The impure product containing about 7% of deuterium, heavy water vapor, and small amounts of higher hydrocarbons was purified first by condensation at 57° K. (in a trap cooled by the evaporation of nitrogen at a pressure of 2 to 3 cm. mercury) followed by a short period of evacuation to remove noncondensable gases, and finally distillation from a vessel at 77° K. to another at 57° K.

Methane was prepared by passing > 99% CH_4 from a cylinder through a purification train consisting of copper at 400° C., calcium chloride, ascarite,

phosphorus pentoxide, and glass wool followed by a distillation procedure as with methane- d_4 . Hydrogen was purified by passing electrolytic hydrogen from a cylinder through the same purification train.

Reaction Mixtures

For the experiments according to Procedure A the composition was: 200 cc. CH_4 , 200 cc. CD_4 (6.4% CD_3H or 98.4 atom % D) and 14.9 cc. argon. For Procedure B, it was 255 cc. CH_4 , 302 cc. CD_4 (7.6% CD_3H or 98.1 atom % D) and 19.9 cc. argon.

Apparatus

The gases were circulated by thermal syphon over a pelleted catalyst placed in a vertical reactor and supported on a perforated glass cup. Two traps kept at $-78^\circ C$. protected the catalyst at all times from mercury vapor. The volume of gas between the exit stopcock and the cold traps was kept to a minimum in order that samples would be representative of the circulating gas. The total volume of the reactor was 215 cc.

The reactor was placed inside an air thermostat whose temperature was automatically controlled by a special regulator which eliminated temperature changes due to changes in barometric pressure. While there was a vertical temperature gradient within the reactor, regulation to within $0.3^\circ C$. at the catalyst was secured, at all temperatures employed between 100° and $400^\circ C$.

The mass spectrometer was of the Nier type (4) with a 60° copper tube. A 67 volt-electron, 0.8 ma. total emission, ionizing beam was used. Peaks were located by varying the accelerating voltage. For the studies of carbon removal by hydrogen it was important to have a low, mass 18, background because, in the presence of hydrogen, the H_2O^+ peak is several times larger than when methane or argon is present or when the tube is evacuated. Low, mass 18, backgrounds were obtained by baking at $300^\circ C$. in 1 atm. of hydrogen for 24 hr. followed by evacuation at the same temperature for 24 hr., cooling, and continued evacuation with the source at $200^\circ C$., the filament on and hydrogen behind the leak at all times when the instrument was not in use. With such pretreatment, in an analysis at room temperature the water peak decreased to about one-quarter of its value at $200^\circ C$. Thus, the water peak was lowered to 8 cm. when the hydrogen peak was 18,000 cm. so that it was then possible to measure with sufficient accuracy the methane- d_2 peaks. These varied from 0 to 30 cm. on the scale just discussed. Samples were corrected for background by bracketing them with pure hydrogen. The presence of oxygen in a sample markedly increased the water peak, necessitating discontinuance of analysis and baking of the source for some 12 hr.

Interesting fluctuations of the electron emission current were observed since the filament was operated from storage batteries. Argon has no effect. An emission of 0.8 ma. in hydrogen changed to 0.75 ma. on evacuation, returning

to 0.8 ma. on reintroduction of hydrogen. Pure methane lowered the current from 0.8 ma. to *circa* 0.4 ma. with a proportionately smaller decrease if hydrogen was also present.

Catalyst

The catalyst was principally nickel with about 20% of chromium oxide as a support. Twenty cylindrical pellets, weighing 0.9 gm., of apparent volume 0.7 cc. in all were used. The initial reduction of the catalyst was carried out in hydrogen at 400° C.

Experimental Results

A. METHANE-METHANE- d_4 EXCHANGE KINETICS

Evaluation of the Mass Spectrometric Data

The values for the methane- d_4 , methane- d_3 , and methane- d_2 peaks relative to argon (A^+) were obtained as follows:—

(1) Mass 20 was corrected for the portion of A^{++} falling at this mass. The A^{++} peak falls about 3 v. higher than CD_4^+ at 660 v. There were small variations due to observational errors and instrument behavior. The ratio A^{++}/A^+ was 0.104 for the group of experiments according to Procedure A and 0.083 for group B. Any errors in this ratio have a negligible effect on the kinetic results.

(2) Each mass was corrected for the contribution from the ^{13}C isotope using the value of 1.1% for this abundance.

(3) No corrections were made for overlapping peaks. In the 16 to 20 mass range this was estimated from measurements to be 0.1% or less of the adjacent peak.

(4) Mass 18 was corrected for contributions from the cracking of methane- d_4 and methane- d_3 . The measured pattern for methane is given in Table I and

TABLE I
CRACKING PATTERNS OF THE METHANES

Mass	CH_4	CD_4	CD_3H
20	—	100	—
19	—	—	100
18	—	76.3	25.8
17	—	—	50.5
16	100	8.0	4.8
15	76.8	—	3.2
14	11.7	4.0	3.2
13	5.3	—	0.8
12	1.8	1.2	1.2

the patterns given for methane- d_4 and methane- d_3 were deduced from measurements on deuterio-methane containing $> 98\%$ D. The assumption was made that $(CD_3^+ + CD_2H^+)/CD_3H^+$ was equal to CD_3^+/CD_4^+ , which, though not true, was found to be sufficiently accurate for the purposes in question. A similar assumption was made for CX_2^+ and CX_1^+ , where X is D or H. On this basis the π_D factor of Evans, Bauer, and Beach (2), which they calculated to be 0.38 with 55 volt electrons for CH_3D , becomes 0.65 for CD_3H with 67 volt electrons.

(5) It was assumed, without calibration, that the observed ratios, CD_4/A , CD_3H/A , and CD_2H_2/A , were linear with the true ratios. The observed ratios CD_4/CD_3H , etc., were assumed to be equal to the true ratios.

Equilibrium Analysis and Computation

Equilibrium analyses were made in Expt. 8 in Group A and Expts. 10, 11, 12, 13 in Group B. To obtain an equilibrium analysis for experiments which did not reach equilibrium, values from these several experiments were utilized. This device is subject to two uncertainties:

(1) The equilibrium has a small temperature dependence but this is relatively unimportant.

(2) Fluctuations in the behavior of the mass spectrometer caused variations in the 20/40 and associated ratios. For 17 analyses in the B group the ratio $20/40 = 5.82 \pm 0.22$, $19/40 = 0.496 \pm 0.16$, $18/40 = 4.52 \pm 0.19$. Most of the variation is attributed to mass 40, since the ratio 19/20 was much more reliable at 0.0852 ± 0.0015 . The discrepancy is ascribed in part to the capillary leak and obstruction at that point. Thus for 20/40 there was a set of "high" values at 6.18 ± 0.06 and a "low" set at 5.67 ± 0.10 , with no apparent cause for the change.

In spite of these anomalies it was possible, however, to assign reasonable equilibrium values to the experiments which did not reach equilibrium. An alternative treatment based on the more reliable 19/20 ratio assisted in this objective. A plot was made of the 19/20 ratio versus the sum of 19/40 and 20/40 ratios for all the data using both a linear and a semilog scale, to obtain the best curve, from which values of the sum could be read to correct the observed values. Thus, the ratios 20/40, 19/40, and 18/40 were each multiplied by the factor $(19/40 + 20/40)_{curve}/(19/40 + 20/40)_{obs}$. In this way all the data were placed on a common basis. This procedure made more apparent the small temperature dependence of the equilibrium, and permitted the inclusion of this in the assigned values for equilibrium. Data so obtained are designated "adjusted data."

This treatment is not strictly valid. It assumes that 19/20 versus $(19 + 20)$ is the same at all temperatures. It means that the temperature coefficients of the rate-controlling steps in CD_4 , CH_3D , and CD_2H_2 kinetics are assumed

equal, which is probably not true. However, the data thus plotted do not show a temperature dependence.

Kinetic Data

The assembled data were plotted according to the first order relations: $\log (CD_4 - CD_{4\infty})$ versus t and correspondingly with CD_3H and CD_2H_2 . The times were corrected for the volumes of gas removed for analyses by assuming that the analysis obtained would have required a proportionately longer time interval if no gas had been removed. Methanes are also "removed" by the formation of carbonaceous residues on the catalyst, giving smaller methane/argon ratios. No corrections were made for this factor.

The experimental conditions and data as well as the pretreatment of the catalyst are summarized in Table II for experiments by Procedure A and in

TABLE II
EXCHANGE REACTION. GROUP A EXPERIMENTS

No.	Volume of gas, cc.	Temp., °C.	Time of experiment, hr.	Per cent approach to equilibrium	CD ₄ rate constant K'	
					Unadjusted data	Adjusted data
2 ^a	53.0	150	63	79	0.0098	0.0148
3 ^b	50.0	208	26	77	0.0270	0.0261
4 ^c	50.0	258	18	90	0.0596	0.0600
5 ^d	50.3	207	24	6.5	—	0.0014
6 ^e	51.1	208	24	65	0.0270	0.0277
7 ^f	50.0	208	25	44	0.0122	0.0116
8 ^{g,h}	42.0	258	11½	100 in ~ 5 hr.	0.371	0.359

$$K' = \frac{K}{2.3} = \frac{\Delta[\log_{10} (CD_4 - CD_{4\infty})]}{\Delta t}$$

K' is calculated on the basis of 40 cc. of gas, assuming that $K'_{40} = K'_v \left(\frac{v}{40}\right)$.

Catalyst Treatments:

- ^a 0.9 gm. catalyst, reduced at 400° C. in hydrogen, evacuated 12 hr. at 400° C., washed in CH₄ one hour at 150° C., evacuated. Started (2).
- ^b Adjusted to 208° C. in the gas from (2), evacuated 30 min. Started (3).
- ^c Adjusted to 258° C. in gas from (3), evacuated 5 min. Started (4).
- ^d Adjusted to 208° C. in gas from (4), evacuated 5 min. Started (5).
- ^e Poisoning observed. Evacuated 14 hr. at 208° C., reacted with H₂ at 208° C. for 20 hr. Evacuated 1½ hours at 208° C. Started (6).
- ^f Evacuated 20 min. Started (7).
- ^g H₂ treatment three hours at 208° C., evacuated 12 hr. at 258° C. Started (8).
- ^h H₂ treatment 12 hr. at 208° C. after (8), left in this hydrogen at room temperature.

Table III for those by Procedure B. The catalyst is the same in each group with an interval between the two of seven months, during which time it was maintained in an atmosphere of hydrogen in the reactor at room temperature.

TABLE III
 EXCHANGE REACTION. GROUP B EXPERIMENTS

No.	Volume of gas, cc.	Temp., ° C.	Time of experiment, hr.	Per cent approach to equilibrium	CD ₄ rate constant K' (basis 40 cc.)	
					Unadjusted data	Adjusted data
1	55	138	70	0	—	—
2	54	140.5	97	31	—	0.0022
3	43.8	140.4	139	83	—	0.0060
4	41.7	140.6	331	99	0.0132	0.0121
5	43.1	140.3	89	91	0.0123	0.0120
6	44.1	129.8	188	91	0.0061	0.0060
7	42.9	119.3	520	94	0.0027	0.0027
8	46.1	98.5	513	51	0.00052	0.00064
9	41.9	154.1	65	97	0.0247	0.0247
10	36.6	254.5	15½	100	2.20	2.17
				in ~ 1.5 hr.		
11	36.0	232.7	12½	100	1.115	1.110
				in ~ 3 hr.		
12	35.2	212.9	21½	100	0.499	0.502
				in ~ 7 hr.		
13	38.7	188.5	20	100	0.175	0.174
				in ~ 20 hr.		

Notes:

- (1) No measurable reaction observed in Expt. (1).
- (2) Preceding Expt. (1), catalyst was held at 210° C. for three hours in the hydrogen left on after Expt. A (8), then evacuated at 210° C. Hydrogen treatment at ~ 400° C. according to Procedure B preceded Expts. (2) to (13.)
- (3) Reactor cold traps were at 0° C. for Expts. (1) and (2), and at - 80° C. for (3) to (13).

 CD₄ Data

The CD₄ plots were linear, the adjusted data showing smaller deviations from the line than the unadjusted. Slight curvature in the direction of slower reaction was assumed to be indicative of the onset of poisoning. Fig. 1 shows the plot of $\log k'$ versus $1/T$ for the two groups of experiments. The numbers refer to the experiment numbers, giving the order in which they were done. The Group A experiments fall into two groups, (1) with an activation energy of 4.5 kcal. between 150° and 208° C. and (2) with an activation energy of 26.1 kcal. between 208° and 258° C. It was thought that this might be due to a shift in the dissociative adsorption of methane from $\text{CH}_3 + \text{H}$ at the lower temperature towards $\text{C} + 4\text{H}$ in the higher temperature range. It emerged that the results were affected by catalyst poisoning, probably carbon, the formation of methane by hydrogen treatment at 208° C. confirming this.

It is also shown by a comparison of Expts. 3 and 6 of Group A with Expts. 12 and 13 of Group B that hydrogen treatment at 208° C. for as long as 20 hr. did not remove all the poison, that some was still retained on sites active in catalyzing the exchange.

In the experiments of Group B with preliminary hydrogen treatment at 400° to 420° C. the $\log k'$ versus $1/T$ plot was linear over the whole temperature range, 100° to 255° C., with an activation energy of 20.9 kcal., in good

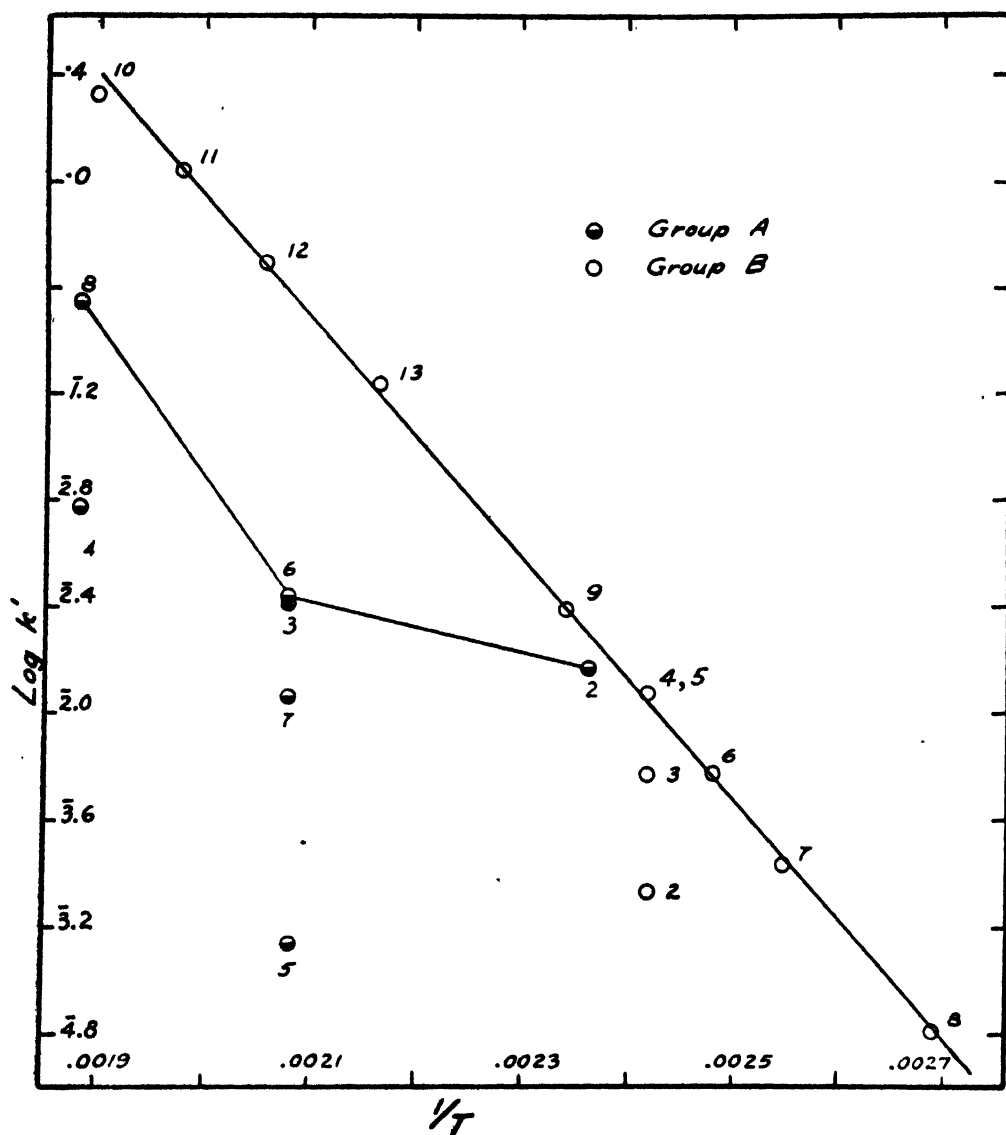


FIG. 1.

agreement with the value of 19 kcal. obtained by Morikawa, Benedict, and Taylor between 138° and 255° C. For all points except that of Expt. 10, the straight line fit was good. In the case of Expt. 10, k' was low, with indications on the plot of $\log (CD_4 - CD_{4\infty})$ versus t that thermal circulation of the gas was beginning to limit the rate.

In the initial experiments of Group B the activity was low, possibly owing to mercury poisoning since the cold trap in B (1) was at 0° C. instead of

— 80° C., or possibly owing to carbon poison in a form only slowly removed at 400° C. (see below). There is also a possibility that adsorbed hydrogen was covering the most active centers.

CHD₃ and CH₂D₂ Data

The methane- d_3 and - d_2 data yielded a first-order plot. These data are less certain than the CD_4 data since they are more sensitive to errors. A percentage error on CD_3H_∞ or CD_3H , and similarly for the - d_2 compound, produces an increasingly greater percentage error in $(CD_3H_\infty - CD_3H)$ as equilibrium is approached. In the case of the $(CD_4 - CD_{4\infty})$ the percentage error is roughly equal to the percentage error in CD_4 . These variations are due to the low equilibrium value for $CD_{4\infty}$ and the large values for CD_3H_∞ and $CD_2H_{2\infty}$. Relative to the argon peak, A^+ , the initial and equilibrium peaks are

	CD_4	CD_3H	CD_2H_2
Initial	5.81	0.49	0.01
Equilibrium at 230° C.	0.69	2.65	4.8

For these reasons the results with methane- d_3 and - d_2 are most reliable in the early stages of the experiments. Fig. 2 for Expts. B (8), and B (9) at 98.5, and 154.1 gives the rate curves drawn from the adjusted data. The same conclusions are derivable from the unadjusted data.

The initial divergence of the curves in B (8) is real since any errors would influence the slope of both methane- d_3 and - d_2 in the same direction. The initial - d_2 slope is slower than the - d_3 slope. These slopes are in qualitative agreement with an assumption of consecutive reactions, $CD_4 \longrightarrow CD_3H \longrightarrow CD_2H_2$, with a temporary "accumulation" of CD_3H . The fact that CD_2H_2 approaches equilibrium more slowly than CD_3H suggests its stepwise formation from CD_4 and CD_3H , the second dissociative step $CD_3 \longrightarrow CD_2 + D$ being slow relative to recombination steps $CD_3 + D$ and $CD_3 + H$, thus requiring a second adsorption step $CD_3H \longrightarrow CD_2H + D$ and a recombination step $CD_2H + H$ to form a CD_2H_2 molecule. A parallel situation would occur beginning with CH_4 . As reaction proceeds the CD_3H slope becomes less than the CD_4 slope. This can be understood in this manner, that the desorption step $CD_3 + H \longrightarrow CD_3H$ is slower than the adsorption step $CD_4 \longrightarrow CD_3 + D$, the former controlling the rate of formation of CD_3H , the latter the disappearance of CD_4 .

B. REACTION OF HYDROGEN WITH SURFACE RESIDUES

The conditions for the treatment of the catalyst surface after the exchange reaction with hydrogen to remove the adsorbed residues, and the experimental results obtained are assembled in Table IV. Pressure after evacuation was measured with a McLeod gauge placed at the entrance to the reactor. Mass

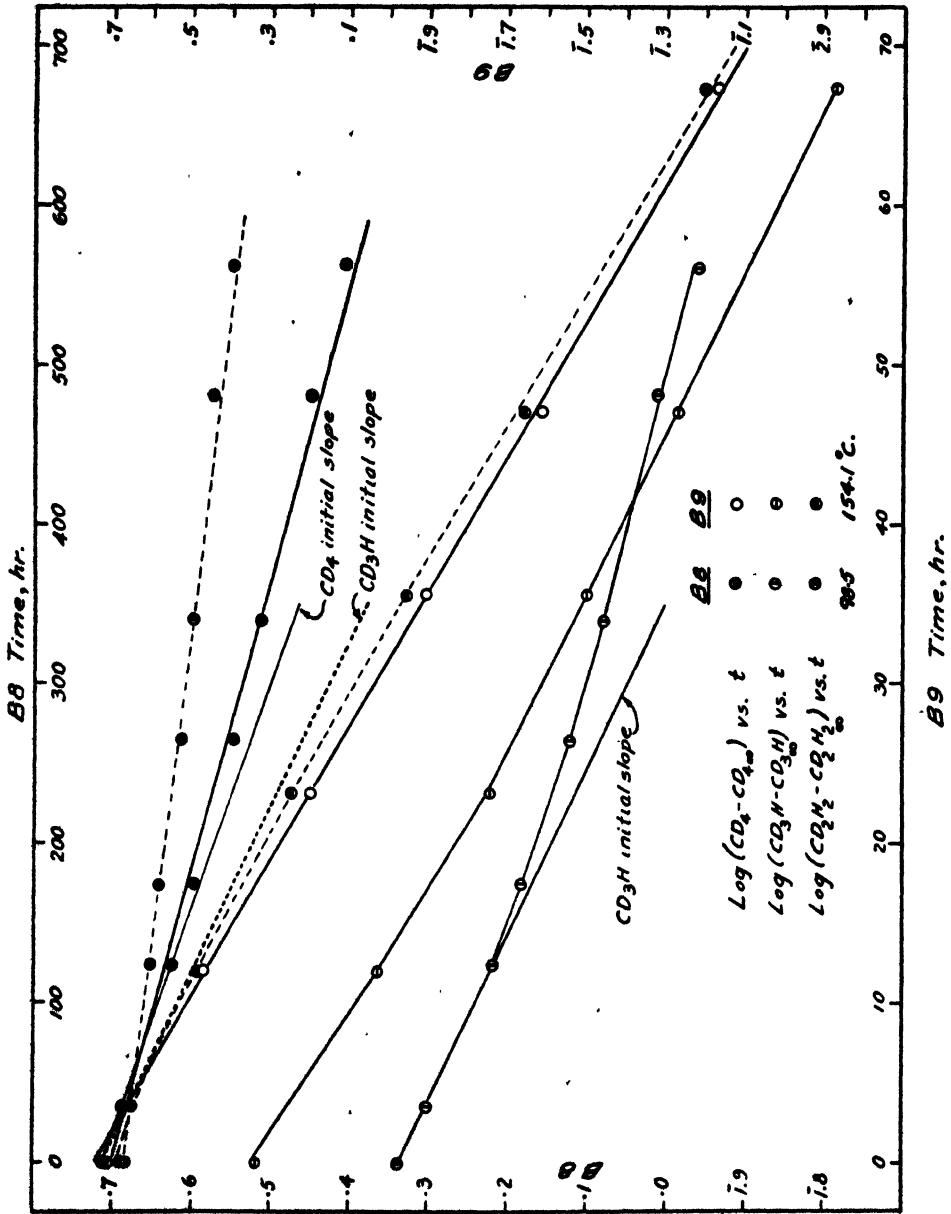


FIG. 2.

TABLE IV
HYDROGEN TREATMENT OF CARBONACEOUS RESIDUES

No.	Evacuation procedure			Removal of surface residues with H ₂				Volume of methanes removed in 1 hr. as peak heights relative to H ₂ = 20,000 (Basis 30 cc. of H ₂)				Relative methane concentrations after 1 hr.			
	Time, hr.	Temp., ° C.	Press., mm.Hg. X 10 ⁻⁴	Time, hr.	Per cent of methanes removed below 400° C.		Total methanes removed, cc.	CH ₄	CDH ₃	CD ₂ H ₂	CD ₃ H	CH ₄	CDH ₃	CD ₂ H ₂	CD ₃ H
					Temp., ° C.										
B (8)	‡	99	8	15 4 4 12‡ 6	99.6 141 49 197 266 400	32 49 58 75	1.6	328	14.2	1.5	Trace	95.5	4.1	0.5	Trace
B (7)	1‡	119.5	—	66 13 2 8	120.5 208 258 400	32 49 63	1.9	518	30.9	2.8	Trace	93.9	5.6	0.5	Trace
B (6)	‡	130	16	51 4	130.6 405	55	1.8	652	50	8	Present	91.8	7.1	1.1	Present
B (5)	2‡	140	—	21‡ 4	141.5 395	56	1.8	793	59	6.9	—	92.3	6.9	0.8	—
B (4)	2‡	141	—	2 1 4	141 350 400	(63) (100) No sample	1.6 to 350° C.	910	71	7	1	92.0	7.2	0.7	0.1
B (9)	‡	154	12	1 2	155 400	67	1.3	897	84	8.1	1	90.6	8.5	0.8	0.1
B (13)	1	190	7	1 2	190.2 400	80	1.4	1160	137	12.4	1	88.5	10.5	0.9	0.1
B (12)	‡	213	12	1 17	214 400	84	1.7	1396	199	18.9	1.9	86.4	12.3	1.2	0.12
B (11)	‡	234	12	1 2	235 400	87	1.9	1580	264	30.6	3.0	84.1	14.1	1.6	0.16
B (10)	‡	256	12	1 3	256 400	83	2.4	2074	145	16.7	4.1	92.6	6.5	0.7	0.18
A (5)	14	208	—	20	208	—	2.2 at 208° C.	—	—	—	—	87*	10	3	—

* After 20 hr.

spectrometer data were corrected for background, mass ^{13}C , and the cracking of CD_2H_2 and CDH_3 , and adjustments were made for the hydrogen and methanes removed in the samples.

The most interesting result, shown in Column 5, is not only that CD , CD_2 , and CD_3 radicals are present with C on the catalyst surface, but also that their concentrations relative to C increase with temperature. There is also indication of a slight increase in the ratio CD_2/CD with temperature.

The absolute concentrations of radicals on the surface increase with temperature. Thus, between 100° and 235°C ., the CD and CD_2 concentrations increase about 20-fold, concentration of C about 5-fold. There is also a definite, though numerically uncertain increase in CD_3 . The only experimental result in the whole series which is at variance with these generalizations is B (10), which will be discussed later.

Rate curves for removal of radicals are shown in Fig. 3. For these curves, methane formed from CH and CH_2 on the surface is subtracted from the methane peak and added to the CDH_3 and CD_2H_2 peaks. This adjustment

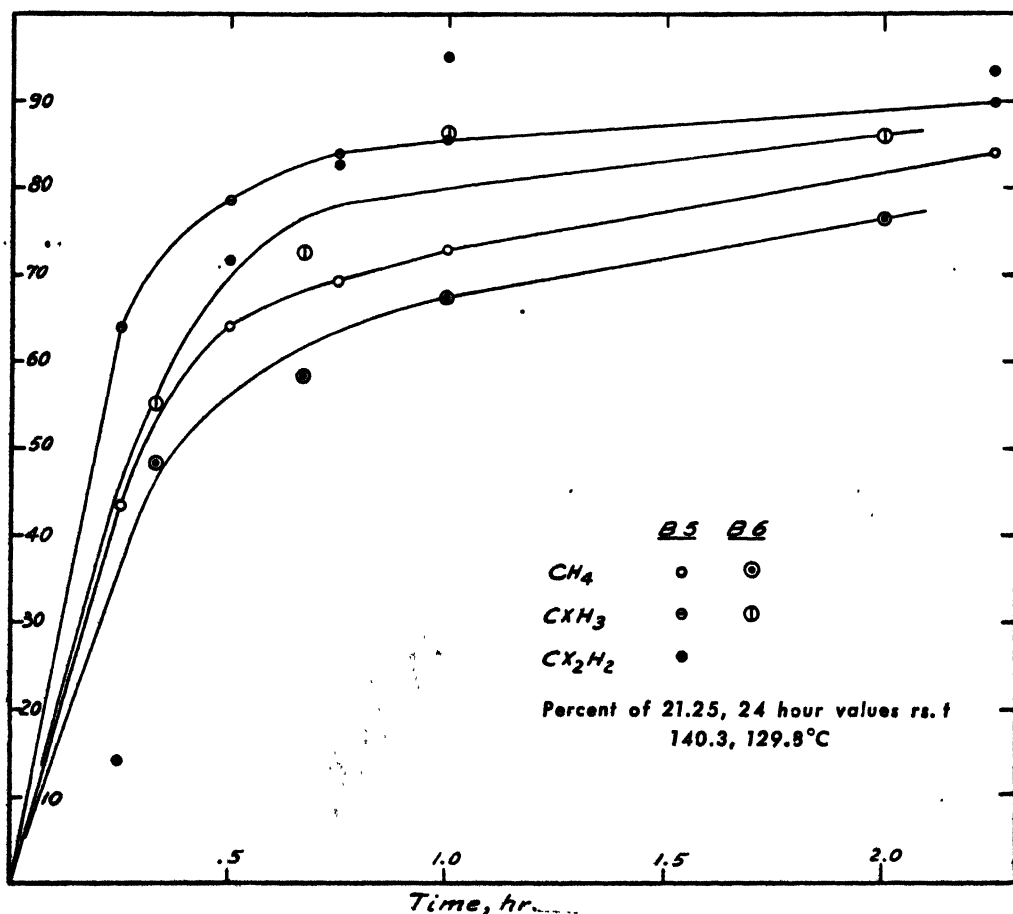


FIG. 3.

is based on the assumption that the relative amounts of CH and CD, CH_2 and CD_2 are equal to the H-D ratio in the methane exchange reaction mixture and that they react at the same rate with hydrogen.

In the case of B (5) at 141.5°C . the percentage values of the total recovered in 21.25 hr. are plotted as a function of time. Of the C recoverable in that time, 73% was obtained in the first hour, while 85% of the CX (where $X = H + D$) was recovered in the first hour. For B (6) at 130.6°C . the corresponding figures were 67 and 80%. While the data show a greater scatter, CX_2 appears to be removed more easily than CX.

Fig. 4 shows the effect of temperature on the rate of removal. For B (8), beginning at 100°C ., the temperature was increased in three stages to 266°C . over a period of 36 hr. The data indicate, though the points are sparse, that

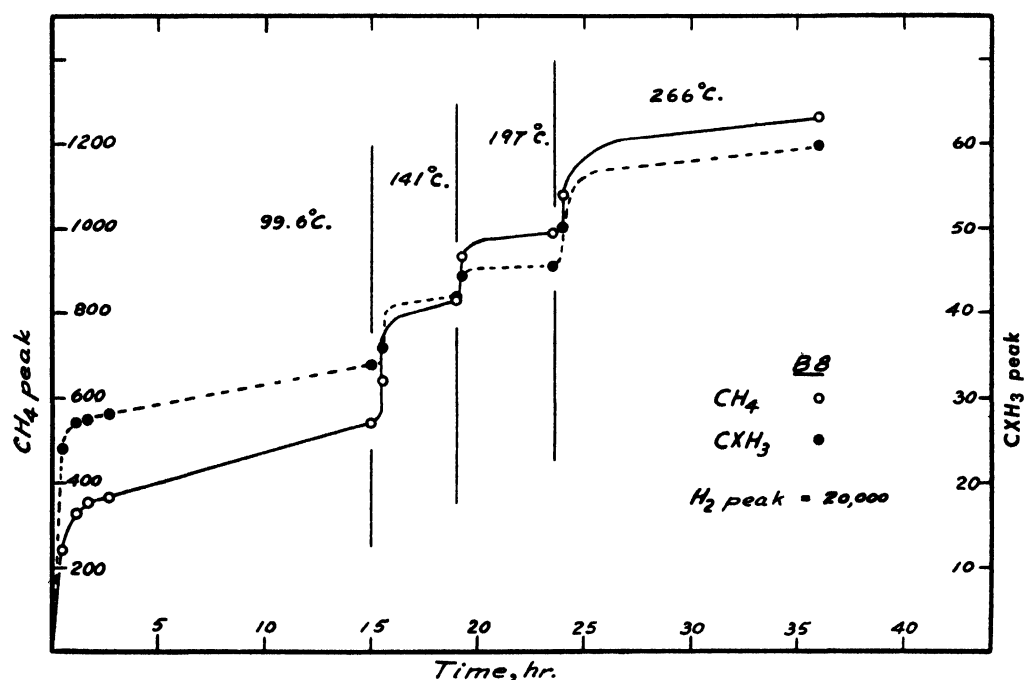


FIG. 4.

each temperature increase caused a sharp increase in the rate of removal not only of C but also of CX. The rate of removal of CX is again the more rapid; a larger fraction of the total comes off more quickly and at a lower temperature than with adsorbed C.

Some possible complicating factors should be noted. (1) It is assumed that adsorption equilibrium is attained. This is probable since the primary step is $CH_4 \rightarrow CH_3 + H$, and C is always found. In B (5) and B (4) at 140°C . where the exchange reactions ran for 89 and 331 hr. respectively the relative CDH_3 concentrations were practically identical. (2) Rate of removal and isotopic exchange may influence the results. If each species on the

catalyst surface reacted at the same rate with hydrogen the relative amounts on the surface would be given by the analyses of the received methanes. It is known, however, that CX and CX₂ are removed more rapidly. Increased reaction time for C removal introduces the possibility of the exchange reactions $H_2 + CDH_3 = HD + CH_4$ and $CH_4 + CD_2H_2 = 2CDH_3$. Although these are slow in the presence of hydrogen some reaction will occur in the direction of lower CDH₃ concentration. The temperature dependence also complicates the picture. We have selected the one-hour waiting period arbitrarily but probably it yields a close approximation to the actual conditions on the surface. It does give the relative concentrations of radicals of approximately the same activity. (3) The time consumed in the methane-exchange reaction also influenced the results. The longer the reaction time the greater the production of a less active carbonaceous material. This is clear from comparison of B (8) after 513 hr. at 98.5° C. with B (13) after 20 hr. at 188.5° C. (4) Evacuation preceding hydrogen treatment from 0.5 to 2.5 hr. has no appreciable effect. The CX, CX₂, and CX₃ radicals are strongly held.

In B (10) at 256° C., which is abnormal, the methane reaction mixture was on the catalyst a proportionately much longer time after equilibrium was reached and so carbon deposition could continue relatively longer. The progressive dissociation to form C leaves fewer sites for further adsorption of methanes and so the absolute concentrations of CD₃, CD₂, and CD would continuously decrease. The dissociation equilibrium would not be altered. The ratios CD₃/CD₂ and CD₂/CD would be unchanged. This is what the data show. The exchange reaction time is therefore another complicating factor.

We discount the importance of isotope exchange between radicals such as $CD + H = CH + D$ in presence of the large excess of hydrogen. We have grounds also for the conclusion that reaction of adsorbed deuterium with carbon on the surface is not an important factor in producing deuterated methanes.

General Discussion

The results obtained both in the methane exchange reaction and in the reaction of hydrogen with surface residues strengthen the concept of a dissociative adsorption process operating in hydrocarbon reactions on catalytic nickel surfaces. The existence of *all* the various dissociative fragments, CD₃, CD₂, CD, C, CH, CH₂, and CH₃ on the surface is immediately suggested by the experimental results. In previous work in this field there has been a tendency to speak of the residues on the surface of the catalyst as carbon. Beeck and his coworkers (1) have frequently referred to such adsorbed materials as "acetylenic" residues indicating a composition approximating (C-H)_n. The present studies lead to the conclusion that all the various possible carbon-hydrogen fragments may be present.

The temperature dependence of the relative radical concentrations indicates that, at higher temperatures, with a given carbon-hydrogen ratio on the surface, the equilibrium shifts in the direction of more highly hydrogenated carbonaceous fragments, i.e., larger values of i for CD_i or CH_i . Assuming an equilibrium distribution of the adsorbed fragments it is evident that this demands an exothermic reaction in the general case $CH_{i+1} = CH_i + H$ in the direction as written or with the corresponding deuterio-reactants. This in its turn depends on the heats of adsorption of CH_i , H , and CH_{i+1} on the given surface as well as on the strength of the CH bond formed in reaction. These several adsorption values will be a function of the metal employed as catalyst. From this point of view it would be important to compare the catalytic metals iron, cobalt, ruthenium, and nickel, all of which have been employed in Fischer-Tropsch processes of production of hydrocarbons from carbon monoxide and hydrogen.

The stepwise character of the removal of carbonaceous residues by hydrogen as the temperature is raised constitutes additional strong evidence of the heterogeneous character of the nickel catalyst employed. Radicals of different reactivities are obviously present. Also, with time, there is a slow transformation of radicals to less reactive species. This is most likely to be true of carbon, and this feature is obvious throughout all the experiments presented.

Two factors, rate and equilibrium, will be operative with a given catalyst over a range of temperatures. At those low temperatures where dissociative adsorption is actually occurring in the case of methane, the CX_3 concentration could be high owing to the slowness of the further dissociation steps. At higher temperatures CX_2 , CX , and C would play an increasing role until, at temperatures where the surface dissociation processes are in rapidly established equilibrium, the thermodynamics of the equilibria will be controlling as to concentrations. In the case of the methane exchange at these temperatures the desorption process $CX_3 + X \longrightarrow CX_4$ and the equilibria will control the rate. In the more complex reactions of the Fischer-Tropsch synthesis the nature of the received products will again be controlled by the two factors of rate and equilibrium here discussed, but in the reverse direction from adsorbed carbon and hydrogen atoms by processes of association. We shall deal with such problems in more detail in subsequent publications.

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EXPERIMENTS ON THE PHOTOLYSIS OF AQUEOUS SOLUTIONS OF CHLORINE, HYPOCHLOROUS ACID, AND SODIUM HYPOCHLORITE¹

BY K. W. YOUNG AND A. J. ALLMAND

Abstract

The photodecompositions of aqueous solutions of chlorine, hypochlorous acid, and sodium hypochlorite have been studied under a variety of conditions involving a wide range of pH, with particular attention paid to the quantum efficiency and to the proportions of the products. Reaction schemes are suggested to account for the results.

1. Introduction and Experimental

The above reactions had all been worked on in this laboratory (1, 2, 3) before the work described below was commenced. The original intention in taking them up again was merely to make a study of the temperature coefficients of quantum yield. The new results, however, differed in detail considerably from those of the former workers, and the scope of the experiments was correspondingly extended. As a consequence of the improved methods employed, the data which follow are presented with some confidence.

Of the sources of error in the older experiments which affected the results, one is conjectural, viz., over-neutralization of hypochlorous acid with caustic soda when preparing solutions of sodium hypochlorite. We found that a small excess of alkali lowered the quantum efficiency very considerably, and considerable care was taken in this respect. In addition, two definite improvements in technique were introduced. Losses during the handling of chlorine water by an ordinary Jahowkin pipette were reduced to a very low figure by the use of high accuracy pipettes designed by Mr. H. N. Ridyard, of which Type I has been described elsewhere (9). Further, in the quantum efficiency measurements, the methods already described (4) in connection with the photoreaction between iodine and potassium oxalate were employed, the small quartz cell containing the photolyte and also the cased thermopile being immersed in a thermostat, with great gains both in accuracy and reproducibility.*

Little need be added about the experimental methods used. Hypochlorous acid was prepared by the method of Taylor and Bostock (10), chlorine was taken from cylinders, and all other reagents were of A.R. quality. All three photolytes give chloric acid (or chlorate) and oxygen, to the exclusion of other products, and the main experiments comprised the study of the effects of variations in experimental conditions on (a) the percentage of chlorine (hypochlorous acid, sodium hypochlorite) which reacted to give chloric acid

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Contribution from University of London, King's College, London, England.

* The absolute absorbed intensities were of the order of 0.1 to 2 gm-cal. per hr., or say, $1-20 \times 10^{18}$ quanta per hour, depending on the wave length and on concentration.

(chlorate) as a product and (b) the quantum efficiency. In the case of chlorine water, the majority of the "chlorate percentages" were determined at room temperature, using the full light of the quartz-mercury lamp and quartz flasks cooled by a stream of tap water, but when using HClO or NaClO , the flasks were immersed in a thermostat. When determining chloric acid, unreacted chlorine (HClO , NaClO) was estimated by warming with a known volume of standard alkaline sodium oxalate solution, acidifying with sulphuric acid, and titrating the excess of oxalate with KMnO_4 . Appropriate experiments showed that chlorate was neither formed nor removed by this treatment. A known volume of standard ferrous sulphate was then added, the mixture boiled in an atmosphere of carbon dioxide, and the excess of ferrous iron back-titrated.

2. Results. Percentages of Chlorate Formed in Reaction

(a) Chlorine Water

With solutions of initial concentration 0.018–0.085 M , in the full light of the quartz-mercury lamp in quartz vessels at room temperature, the % ClO_3 varied between 62.2–64.1 for 95–100% decomposition. For 74–80% decomposition, the figures were 61.6–62.4%. The indication that the % ClO_3 may fall with diminishing degree of photolysis is amply confirmed by the following results:

% Decomposition	32.1	26.7	22.4	19.7	14.5	11.0	10.8
% ClO_3	57.1	52.4	45.3	45.6	40.9	33.4	29.1

A rise in temperature slightly increased the % ClO_3 . Thus, for 93–97% decomposition, the figure was 65.6 at 25° and 66.7 at 30° C.

A few experiments were carried out in glass vessels, and therefore with absorbed radiation of considerably longer average wave length. With solutions of the same concentration range as above, the following results were obtained:

% Decomposition	20.6	18.5
% ClO_3	37.0	30.4

Comparison with the above figures indicates a lower % ClO_3 in light of longer wave length. Two other experiments were carried out in glass vessels, using very dilute solutions of chlorine, decomposed to completion.

Concentration of chlorine	0.00127 M	0.00186 M
% ClO_3	35.5	27.8

Undoubtedly, the lower concentration of chlorine as well as the use of light of longer wave length have co-operated here in reducing the % ClO_2 from the figure of 62–64 previously found for a degree of decomposition exceeding 95%.

Experiments in which chlorine water (0.028 *M*) was insolated in quartz vessels in the presence of 0.5 *N* alkali-metal chloride (KCl , NaCl , LiCl) to 73–80% decomposition, showed indications of a slight lowering in % ClO_2 (59.5–61.5). On the other hand, the effects of added HCl were very marked, if somewhat complex.

With moderate additions of HCl (Cl_2 , 0.045–0.068 *M*; HCl , 0.055–0.068 *N*) and with 85–97% decomposition, the % ClO_2 was 64.7–65.9, slightly higher than in the absence of HCl . With concentrations rather outside these limits, figures of 65.7–67.8 were recorded. As before, they fell with decreasing degree of decomposition.

Cl_2 , <i>M</i>	HCl , <i>N</i>	% Decomposition	% ClO_2
0.0507	0.065	27.0	52.5
0.0458	0.065	25.0	45.5
0.0517	0.065	19.0	43.8

Very small quantities of added HCl sufficed to cause this increase.

Cl_2 , <i>M</i>	HCl , <i>N</i>	% Decomposition	% ClO_2
0.0650	0.00913	95.2	65.3
0.0527	0.00913	99.2	69.5

Under identical conditions in the absence of HCl , the % ClO_2 was 62.7–63.4. Larger amounts of HCl on the other hand lowered the % ClO_2 .

Cl_2 , <i>M</i>	HCl , <i>N</i>	% Decomposition	% ClO_2
0.0625	0.154	64.6	59.1
0.0477	0.196	41.6	49.9
0.0515	0.243	44.4	32.5
0.0222	0.340	77.9	24.0
0.0395	0.850	51.0	7.3
0.0521	1.91	75.1	1.9

(b) Hypochlorous Acid

A few measurements only were done with unbuffered solutions of the acid. Concentration had no appreciable effect between 0.0362–0.0704 *M*. In two cases where the solution was completely decomposed, % ClO_2 was 58.3. It fell off with decrease in degree of decomposition—thus 51.3 at 62% decomposition.

A number of experiments were done with solutions buffered with Na_2HPO_4 , in order to keep down the H^+ ion concentration, and hence the formation of chlorine.

Na_2HPO_4 , M	HClO , M	$\text{Na}_2\text{HPO}_4/\text{HClO}$	% Decomposition	% ClO_3
20° C.	0.109	4	95	68.9
	0.152	3	96	70.7
	0.152	1.75	85	79.2
	0.326	12	100	64.2
	0.326	11	100	66.5
	0.326	11	67	66.9
30° C. 0.326	0.0261	12.5	99	66.2

The % ClO_3 values are considerably higher than with unbuffered solutions, and increase with decreasing $\text{Na}_2\text{HPO}_4/\text{HClO}$ ratio.

Experiments in presence of 0.5 N KCl (or NaCl or LiCl) gave % ClO_3 values of 56–62 for 80–100% decomposition, i.e., a definite decrease.

Two experiments with solutions of 0.0289 M HClO + 0.278 M NaH_2PO_4 gave 50 and 53% ClO_3 , for 46 and 62% decomposition, respectively, values similar to those obtained with the unbuffered acid.

(c) Sodium Hypochlorite

The few experiments done are summarized below. In all cases, the NaClO concentration was 0.022–0.026 M , and the percentage decomposition 86–99%.

Light used	Temperature, ° C.	Added NaOH	% ClO_3
Full radiation	20	None	65.1–69.0
do	30	do	65.7
3655 Å	20	do	72.2–74.0
Full radiation	20	5% excess	63.7
do	20	100% excess	46.9–48.5

The most obvious effect is that of the addition of alkali. The use of light of shorter average wave length increases the value of % ClO_3 , as with chlorine water. On the other hand, any effect of temperature rise is negligible.

3. Results. Quantum Efficiencies

(a) Chlorine Water

Preliminary experiments with the full light of the lamp, in which the intensity was varied in the ratio of 6 : 3 : 2 : 1 by means of carefully applied metal gauzes, the times of exposure being altered in the inverse ratio, showed

that the rate of reaction was proportional to the incident intensity within the experimental error.

The majority of the runs were carried out at 20° C., using radiation of wave length 3655 Å. In view of the necessarily low intensities, the percentage decompositions were considerably less than was usually the case when determining the % ClO₂ values, and no systematic connection could be traced. On the other hand, the values of γ undoubtedly were lower the lower the concentration of chlorine.

Cl ₂ , <i>M</i>	% Decomposition	γ
0.021–0.039	10–25	0.84–0.99
0.0054–0.013	14–19	0.78–0.79

The addition of HCl lowered the quantum efficiency, to an extent increasing with its concentration. As in absence of added HCl, γ fell off as the chlorine concentration was decreased.

Cl ₂ , <i>M</i>	HCl, <i>N</i>	% Decomposition	γ
0.028–0.042	0.00391	12	0.76
	0.0195	9	0.65
	0.0235	11	0.59
	0.0236	5	0.54
	0.118	13–15	0.24–0.26
0.0423	0.118	13	0.26
0.0358	—	15	0.24
0.0123	—	23–24	0.17–0.20
0.00724	—	27	0.18

The addition of 0.5 *N* alkali-metal chloride also lowered the quantum efficiency very considerably, but to a lesser degree than HCl. For about 8% decomposition of 0.0342 *M* chlorine water, the γ values were respectively, for solutions containing KCl, NaCl, and LiCl, 0.27, 0.34, and 0.38. The effect of wave length was marked.

Wave length, Å	Cl ₂ , <i>M</i>	% Decomposition	γ
4348	0.0285–0.0372	6.6–7.8	0.41
3655	0.0302	18	0.90
3129	0.0372	11.4	1.94

The temperature coefficients of quantum efficiency were determined over the range of 20°–30° C., including some measurements with 3655 Å on solutions containing some added HCl. The results were as follows.

Wave length, Å	Cl ₂ , M	HCl, N	γ_{30}/γ_{20}
4348	0.0170	—	1.46
3655	0.0170	—	1.40
3129	0.0170	—	1.11
3655	0.0147	—	1.42
	0.0147	0.076	1.53
	0.0147	0.108	1.60

(b) *Hypochlorous Acid*

No measurements were made on unbuffered solutions. With added Na₂HPO₄, the following results were obtained (3655 Å; 20° C.).

Na ₂ HPO ₄ , M	HClO, M	Na ₂ HPO ₄ /HClO	% Decomposition	γ
0.00435	0.00138	3.2	22	0.83
0.108	0.0370	2.9	12	1.96
0.217	0.0370	5.9	11	1.94
0.320	0.0241	13	11	1.46
0.320	0.0270	12	15	1.64
0.320	0.0370	8.6	10–13	1.63

The first experiment clearly brings out the effect of the very low concentration of HClO. The other results show that as the ratio Na₂HPO₄/HClO becomes less, γ rises, as also does the % ClO₂ (for higher degrees of decomposition). Experiments with added 0.5 N KCl and 0.5 N NaCl gave γ values of 1.96 and 1.93 with a Na₂HPO₄/HClO ratio of about seven. The effect of the alkali metal halide is thus negligible. A single run with 0.0343 M HClO + 0.326 M NaH₂PO₄ gave a γ value of 1.46.

The temperature coefficients of quantum efficiency were determined between 20°–30° C. for light of 3655 Å and 3129 Å. They were found to be respectively 1.05–1.065 and 1.01–1.02, considerably lower than the values for chlorine water.

(c) *Sodium Hypochlorite*

Experiments with 3655 Å at 20° C. on supposedly exactly neutral solutions of NaClO gave unsatisfactorily reproducible results. With 0.0172–0.0415 M solutions, and % decompositions between the limits 12–25, the γ values fluctuated over the range 1.01–1.40, with no visible systematic dependence on either of these variables. Runs with solutions of NaClO overneutralized by NaOH gave results which probably explain this behavior.

Solution	γ
0.0289 M NaClO	1.18-1.40 (5 runs)
+ 3.3% excess NaOH	1.00
+ 6.9%	0.53
+ 22.7%	0.46
0.0415 M NaClO + 100%	0.44

In confirmation of this view is the fact that solutions buffered with Na_2HPO_4 gave reproducible results.

Na_2HPO_4	NaClO	$\text{Na}_2\text{HPO}_4/\text{NaClO}$	γ
0.108	0.0326	3.3	1.23-1.28 (3 runs)
0.217	0.0447	4.9	1.13
0.118	0.0012	100	0.90

As before, the effect of temperature on γ was determined for 3655 Å and 3129 Å. The ratio γ_{30}/γ_{20} was found to be respectively 1.08 and 1.05 for neutral solutions. For a solution containing 100% excess of added NaOH, the value for 3655 Å was 1.12.

4. Discussion

(a) General

The decadic molecular extinction coefficients of aqueous solutions of chlorine and of hypochlorous acid have been determined by Ferguson, Slotin, and Style (5) and some figures for the ClO' ion were published by Allmand and Webb (3). We made a number of measurements on solutions of Cl_2 , $\text{Cl}_2 + \text{HCl}$, HClO and $\text{HClO} + \text{Na}_2\text{HPO}_4$, and the results were in good agreement with the data referred to. Over the whole wave length region concerned, $\alpha_{\text{Cl}_2} > \alpha_{\text{ClO}'} > \alpha_{\text{HClO}}$. Thus, at 3655 Å, the respective values are about 30, 6.5, and 0.9. In addition, in HClO solutions buffered with Na_2HPO_4 of the concentration used by us, a high proportion (up to 50%) of the original HClO is present as ClO' ions. It follows that, as far as the primary process of light absorption is concerned, our main experiments fall into two groups:—

- (a) those on chlorine water,
- (b) those on NaClO and buffered HClO solutions,

where respectively the Cl_2 molecule and the ClO' ion are the important absorbing constituents, the HClO molecule playing quite a minor role. Even in the few runs done with unbuffered HClO , the absorption of light will essentially be due to chlorine after the reaction has been in course for some

little time. On the other hand, both in unbuffered and also in Na_2HPO_4 -buffered solutions of the acid, HClO will be present as a possible reactant, whilst in the isolated experiments with NaH_2PO_4 -buffered solutions, it will be solely responsible both for light absorption and for subsequent reaction.

The general concordance between the different reactions in respect of the % ClO_3 produced suggests that, subsequent to effective light absorption, the reaction mechanisms are identical, or very similar, in the final stages of the reactions, and, as will be seen, we attribute the production of ClO_3^- ions in all cases to a mechanism involving ClO radicals. Further, the acidity or pH of the reaction medium has a marked effect on both γ and % ClO_3 , and any reaction schemes must necessarily account for the main lines of this effect. Using γ_{365} values, and neglecting any effects of concentration of reactant or of its % decomposition, the results are as follows, where the pH values in buffered solutions are calculated in the usual way from the first and second dissociation constants of H_3PO_4 and from that of HClO .

System	pH	γ	% ClO_3
$\text{HCl} + \text{Cl}_2$	- 0.3	?	1.9
	1.0	0.2	60
	↓	↓	↓
Cl_2	1.2	0.76	67
	1.3 (50% decomposition)	0.90	63
Unbuffered HClO	1.9 (50% decomposition)	?	58
$\text{NaH}_2\text{PO}_4 + \text{HClO}$	5.5	1.46	53
$\text{Na}_2\text{HPO}_4 + \text{HClO}$	7.5	1.94	79
	↓	↓	↓
	8.1	1.64; 1.46 ?	64-66
Neutral or Na_2HPO_4 -buffered NaClO	9.7	1.28	63-69
	↓	↓	
	10	1.13	
Alkaline NaClO	11	1.0	64
	↓	↓	↓
	12.6	0.44	48

Both γ and % ClO_3 have maximum values near the neutral point. It may be mentioned that other workers (ref. (1) and unpublished experiments by H. J. Taylor) found values exceeding 80 for % ClO_3 in Na_2HPO_4 -buffered solutions. γ falls off continuously as the reaction medium becomes either more acid or more alkaline. The % ClO_3 rises from a very low figure at low

pH to what we think is a true maximum in weakly acid Cl_2 solutions, then falls, and must clearly rise rapidly between pH 5.5–7.5 (or 7). It is unfortunate that this particular region was not studied, but the point was not appreciated when the experiments were being done. From its maximum value, % ClO_2 then falls off as the solution becomes more alkaline, with an obvious halt in the region pH 8–11.

The values of some of the bond energies used later are still the subject of discussion. The figures we use are based on standard data, considered in the light of recent papers by Weiss (12, 13) and by Walsh (11). D values of 55 kcal. and 88 kcal. are assumed for the dissociation of aqueous HClO to $\text{Cl} + \text{OH}$ and to $\text{H} + \text{ClO}$ respectively, E for $\text{Cl}-\text{O}$ being taken as 67 kcal. both in the free radical and in HClO . The combined electron affinity plus heat of hydration of the OH' and ClO' ions are respectively assumed to be 152 and 120 kcal.

Finally, one other important experimental result, not referred to in the previous sections, must be mentioned. The earlier workers in this laboratory noticed (1) in many cases oxygen evolution from Cl_2 or HClO solutions after irradiation had ceased. Not being able to correlate this observation, within their somewhat large experimental error, with a decrease in the titer of the solution, they attributed the phenomenon to supersaturation. Careful unpublished experiments by H. N. Ridyard have however shown that a true aftereffect does exist. Thus, in one case, a 0.042 M solution of HClO was irradiated until the titer was 0.0218 M and the % ClO_2 determined. The next day, the titer had fallen further to 0.0178 M , but the chloric acid concentration was unchanged. This type of result was always found when looked for, and is of course evidence of short reaction chains initiated by the light. It should be noted that Kauffmann (8) attributed the very slow spontaneous decomposition of hypochlorite solutions to a similar chain reaction, initiated by HClO , and suggests a mechanism which we shall also employ.

(b) Chlorine Water

The primary reaction here (and the important reaction in unbuffered solutions of HClO after the photolysis has been in progress for some little time) is



The resulting Cl atoms will either recombine, in accordance with the views advanced by Franck and Rabinowitsch (6), by



or will react with water



As a higher separation velocity of the Cl atoms produced in (1) will both increase the probability of (2) and also decrease that of (1'), the yield of OH groups per absorbed quantum will rise with increasing frequency. The endothermicity of (2) will account for the temperature coefficient of the reaction, and for its dependence on the frequency of the exciting light.

The addition of 0.5 *N* alkali-metal halide, whilst having no effect on the % ClO₃, lowers γ very considerably. This is due to

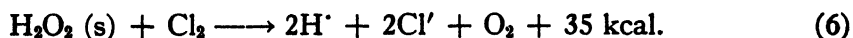
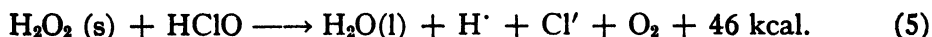
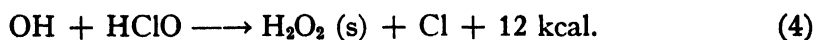


The reaction is endothermic, but the Cl' concentration greatly exceeds those of the other reactants. HCl reacts in the same way, but more strongly, and quite a low concentration has an effect. This is obviously attributable to



The OH radicals (and, to a lesser extent, the Cl atoms) emerging from the primary process then react with the Cl₂ and HOCl molecules, or else sooner or later recombine. Clearly, the lower the Cl₂(HClO) concentration, the more likely will be the latter event and, as would be expected, γ falls off as (Cl₂) decreases.

To understand the role of the OH radicals in initiating further decomposition, the evidence for the evolution of O₂ by a chain reaction must be considered, and attention paid to the facts that (a) a small addition of HCl actually increases the % ClO₃ whilst larger amounts diminish it and (b) the % ClO₃ increases as the % decomposition rises. An examination of the data, taking into account the experimental errors, shows that this second effect is essentially accounted for by a low value early in the reaction, the subsequent stages giving a % ClO₃ of about 67. To explain this result, which appears to be bound up with the relatively high amount of HClO present initially, diminishing as HCl is formed in the photolysis or disappearing if it is added at the start, we suggest the reactions

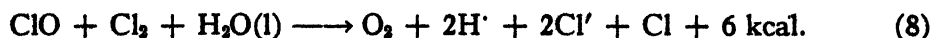


the first of these taking place more easily than any alternative, whether involving Cl atoms or OH groups, which helps the decomposition forward.

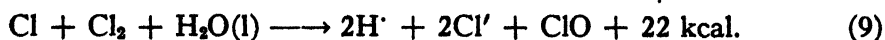
As the HClO concentration falls, the following reaction becomes increasingly more important



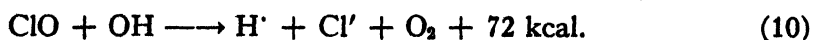
For the ClO radicals resulting from (7), there is the choice of the following reactions—*either*



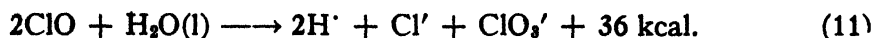
followed by



or



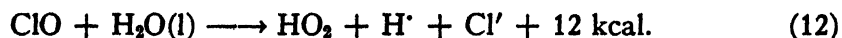
or



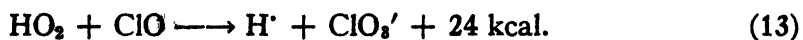
(8) and (9) constitute the slow chain reaction producing oxygen mentioned earlier as responsible for the aftereffect in chlorine solutions. This can of course be initiated by primary Cl atoms (9) rather than by OH groups (7) and this will tend to happen in presence of much HCl. (10) and (11) involve the interaction of two radicals, and will be favored, relatively to (8), the higher the radical concentration. The ratio $[\text{OH}] : [\text{ClO}]$ is kept down by (7), and hence also the rate of (10) compared with the rate of (11).

The result follows that where, for one reason or another, the stationary radical concentrations are low, as with much HCl present or in dilute solutions of chlorine, the % ClO_2 will fall off. These conclusions are confirmed by experiment. On the other hand, both increasing frequency and rise in temperature raise the efficiency of the primary process and consequently also the prevailing radical concentration, which explains the observed increase in % ClO_2 .

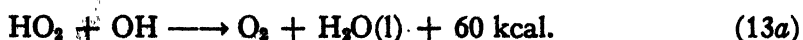
The assumption that ClO radicals participate raises the question of their possible interaction with water—



If this reaction does not take place too quickly, the HO_2 groups can be assumed to disappear by

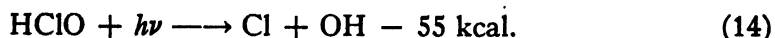


which will make no difference to the % ClO_2 . If, of course, (12) is very rapid, then HO_2 groups can only disappear by reactions giving oxygen, such as

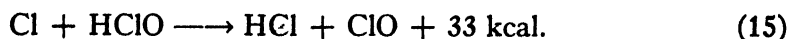


and ClO radicals can no longer be regarded as the source of ClO_2^\cdot ions. We prefer however rather to adhere to our present mechanism than to introduce one involving, for example, successive oxidation of HClO to HClO_2 and HClO_3 .

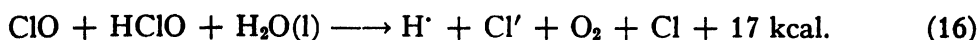
The photolysis of unbuffered HClO is explicable on similar lines.
The primary process will be



followed by (4) leading to (5) and (6) and (we assume) less easily by



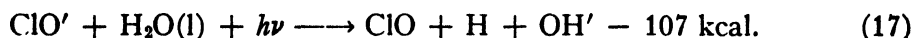
The subsequent chain reaction involves, in addition to (15),



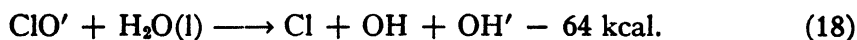
The chain ending processes will be as in chlorine water, the whole sequence of steps will more and more resemble the photolysis of chlorine water as the reaction proceeds, and the % ClO₃ will be similar, but lower, because of the greater relative importance of (4), (5), (6).

(c) *Sodium Hypochlorite and Hypochlorous Acid Solutions Buffered with Disodium Hydrogen Phosphate*

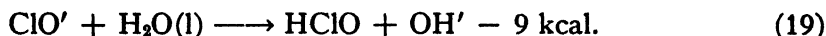
The absorption spectrum of the ClO' ion can be regarded as a modified electron affinity spectrum. The most direct formulation of the primary process would then be



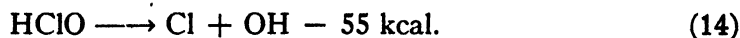
The threshold frequency, corresponding to about 2660 Å, is however far too high, and we suggest instead



proceeding by the coupled steps



and

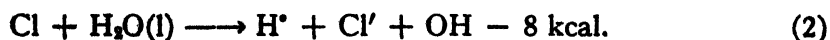


where the threshold is at about 4440 Å.

As is the case, for example, in the photolysis of the sulphites (7) increasing alkalinity diminishes the quantum yield. This effect is clearly due to the re-formation of ClO' ions by the reversal of the primary process

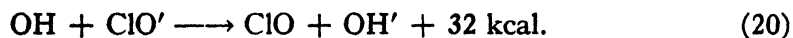


The Cl atoms resulting from (18) will react with water

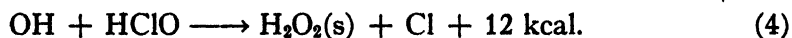


As with chlorine water, both because of this reaction and because of the increased effectiveness of separation at their instant of formation of the primary Cl atoms and OH groups, γ would be expected to increase with rise in frequency of the absorbed light. We actually carried out no measurements of this kind, but the trend of the dependence of the temperature coefficients of the reaction on wave length accords with the existence of such an effect, both for NaClO and for buffered HClO solutions. The rise in the temperature coefficient in the former case as the pH increases is also as would be expected.

The next stage of the reaction we suggest to be

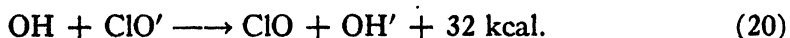
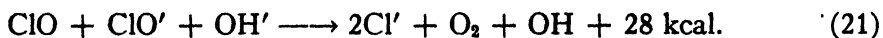


and, where HClO is present



As in the case of chlorine water, the lower the concentration of ClO' and/or HClO, the more likely are the initiating radicals to recombine. We accordingly found γ to fall with decrease in concentration, both for NaClO and for buffered HClO solutions.

Step (20), a mere electron transfer, will be relatively very rapid compared with (4), which can be neglected both in NaClO and in Na₂HPO₄-buffered solutions of HClO. Following on (20), we suggest the chain reaction mechanism already put forward by Kauffmann (8).



The sole chain ending reaction of importance will be (11) thus accounting for the high % ClO₂ found with such solutions of low pH. At higher pH values, the rate of (21) is increased, OH' ions being a reactant, and, owing to the lower efficiency of the primary process, the prevailing radical concentration will fall; both these effects assist towards a lower % ClO₂.

On the other hand, the small positive dependence of % ClO₂ on temperature rise, using buffered HClO solutions, and the very definite positive effect of increasing frequency found with NaClO solutions (where the effect of temperature was inappreciable) are both due to a higher radical concentration arising out of a more efficient primary process.

(d) Hypochlorous Acid Solutions Buffered with Sodium Dihydrogen Phosphate

These few experiments are separately treated as they are the only ones in which HClO is the sole reactant to be considered, and the conditions are therefore relatively simple. The primary process will be (14), followed by (4),

(5), (6), and by the chain reaction (15), (16), initiated by primary Cl atoms, and by those resulting from (4). The sole chain ending reaction of significance will be (11). Oxygen is produced by both (5), (6) and (15), (16). The extinction coefficient of HClO is considerably lower than those of Cl₂ and of ClO' ions, and the stationary radical concentration will therefore be rather small. These circumstances adequately explain the relatively low values both of γ and of % ClO₂.

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ABSORPTION SPECTRUM OF METHYL IODIDE IN THE NEAR INFRARED¹

BY G. HERZBERG AND LUISE HERZBERG

Abstract

The absorption spectrum of methyl iodide in the region 8500 to 25,000 Å has been investigated with an absorbing path of 30 m. and pressures up to 200 mm. A large number of bands have been found most of which can be readily classified as // or \perp bands. An assignment of many of these bands to specific overtones or combinations of the fundamentals is suggested. In a number of instances the splitting of binary or ternary combinations of degenerate vibrations on account of anharmonicity is established and found to be in agreement with theoretical predictions.

A. Introduction

When in a polyatomic molecule a degenerate vibration is multiply excited or when two or more degenerate vibrations are singly excited, a state of higher degeneracy results as long as the vibrations are considered as harmonic. However if the anharmonicity of the vibration is taken into account, there is a splitting into component levels none of which has a degeneracy greater than that of the fundamental vibrations involved. Thus in a molecule of point group C_{3v} a state in which a degenerate vibration of species E is doubly excited ($\nu = 2$) splits into two states of species A_1 and E which have slightly different energies. A state in which an E vibration is triply excited splits into three states of species A_1 , A_2 , and E ; and so forth. [For more details see Herzberg (4)]. The situation is further complicated by the fact that often certain symmetric vibrations have very similar frequencies to those of the corresponding degenerate vibrations. In addition Fermi resonances with the overtones of lower frequency fundamentals may occur. All this results in the appearance of a considerable number of bands for example in the regions of the first and second overtones of the stretching vibrations.

Since no such case has as yet been completely analyzed it seemed worth while to study these overtones in a simple example in which parallel and perpendicular bands (corresponding to A_1 and E upper states respectively) can be readily distinguished. Such a case is methyl iodide.

The infrared absorption spectrum of methyl iodide between $20\ \mu$ and $2.8\ \mu$ has been investigated by Bennett and Meyer (2), Barker and Plyler (1), and Lageman and Nielsen (6). The photographic infrared spectrum below $1.15\ \mu$ has been studied by Verleger (8). The region between 1.1 and $2.8\ \mu$ has been investigated by Moorhead (7), but only with a path length of 30 cm. It is in this region that the first and second overtones of the C-H stretching vibrations lie and in which therefore some information with regard to the splitting mentioned above can be obtained. The present study deals with

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this region, using much greater path lengths. Although further work will be required, at higher dispersion, in order to derive complete vibrational formulae, the material thus far collected seems to warrant a discussion at this stage, particularly since it will be some time before the work can be continued and extended.

B. Apparatus

The spectrum was investigated with the aid of the infrared prism spectrometer built by Dr. G. P. Kuiper (5), at Yerkes Observatory. This spectrometer uses a lead sulphide photoconductive cell as the receiving element. The spectrum is recorded on a Brown recorder. The absorption tube was the smaller of the two multiple reflection tubes described by Bernstein and Herzberg (3). With 20 traversals used throughout for methyl iodide the path length is 30 m. Pressures from 2 to 200 mm. were used.

A dispersion curve for the instrument was constructed from measurements of water absorption lines and helium and mercury emission lines. The water lines served also as internal standards in each run.

C. Description of Spectra, Results

The most characteristic features of the absorption spectrum of methyl iodide in the region considered are the two groups of bands near 6000 and 9000 cm^{-1} corresponding to the first and second overtones of the C-H stretching vibrations. Recordings of these two regions are shown in Figs. 1 and 3. In addition there are very strong absorption bands in the region 4000 to 4800 cm^{-1} and less strong but still fairly prominent bands in the region 6700 to 7600 cm^{-1} . A recording of the latter group is shown in Fig. 2.

In most cases it is readily possible to classify the bands as parallel or perpendicular bands. The parallel bands have two absorption maxima at a distance of about 20 cm^{-1} corresponding to the unresolved *P* and *R* branches. The central *Q* branch is so weak (because of the small ratio I_A/I_B) that in most cases it is not observed. The spacings of *P* and *R* maxima of the // bands agree with those found by previous investigators of the same molecule (see above). The \perp bands are much wider and the succession of *Q* branches of the subbands [see ref. (4)] is partially resolved, the separations being of the order of about 10 cm^{-1} . A good example is the band at 5696 cm^{-1} in Fig. 1, which shows the intensity alternation strong-weak-weak-strong characteristic of a molecule with a threefold axis of symmetry and one set of three atoms of nuclear spin $\frac{1}{2}$. The classification (// or \perp) becomes more difficult in the case of overlapping bands. One band was found at 7505 cm^{-1} (see Fig. 2), which has a very strong central maximum with a shoulder on each side resembling a // band of a molecule for which I_A/I_B is large. We believe that this is actually a \perp band in which the separation of successive subbands is very small. However, the possibility that this band is due to an impurity, while unlikely, has not been definitely excluded.

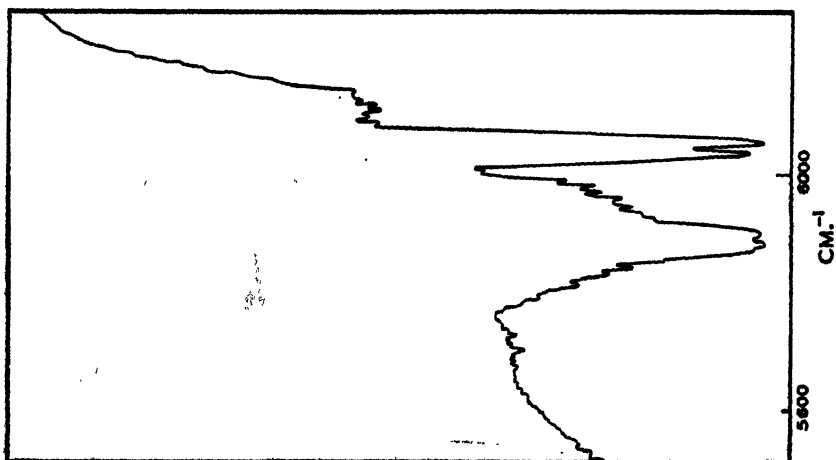


FIG. 1. CH_4 spectrum near 6000 cm^{-1}
(path length, 30m.; pressure, 15mm.).

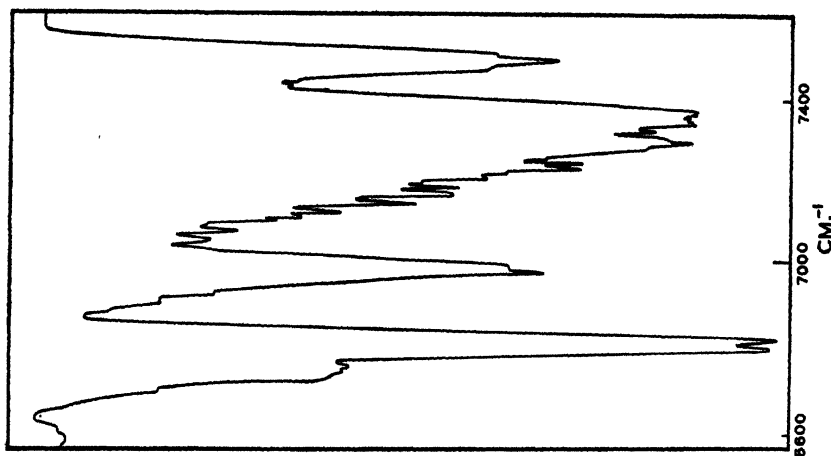


FIG. 2. CH_4 spectrum near 7000 cm^{-1}
(path length, 30m.; pressure, 200 mm.).

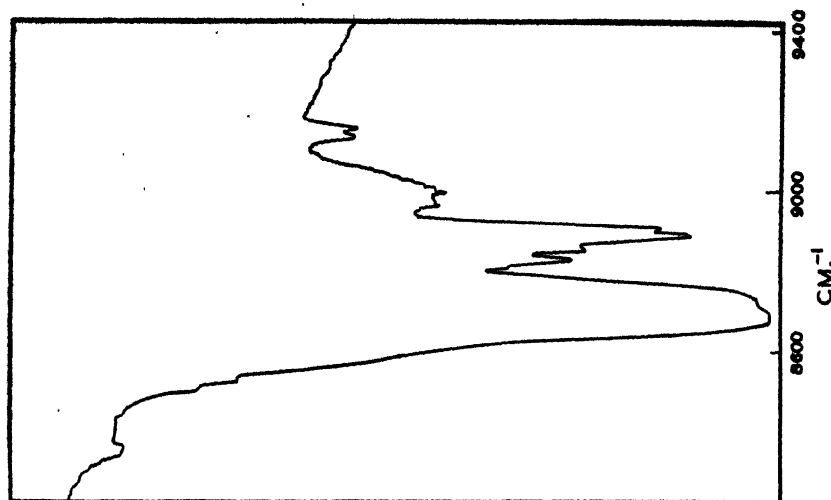


FIG. 3. CH_4 spectrum near 9000 cm^{-1}
(path length, 30m.; pressure, 200 mm.).

Table I gives the observed wave numbers of all the bands measured, with the intensities on a rough scale 0 to 100. The wave numbers should be accurate to about ± 3 cm. $^{-1}$ for the sharp peaks of // bands and ± 10 cm. $^{-1}$ for the centers of the broad \perp bands.

D. Vibrational Analysis

The fundamentals of methyl iodide have been determined by Bennett and Meyer (2) and Barker and Plyler (1). The frequencies of the totally symmetric vibrations are

$$\nu_1 = 2969.8 \qquad \nu_2 = 1251.5 \qquad \nu_3 = 532.8$$

and those of the degenerate vibrations (as corrected by Herzberg (4))

$$\nu_4 = 3060.3 \qquad \nu_5 = 1440.3 \qquad \nu_6 = 880.1$$

Here it must be noted that the totally symmetric component of the first overtone of ν_5 (that is $2\nu_5$) which is observed at 2861 cm. $^{-1}$ resonates with ν_1 so that the frequency of ν_1 is slightly larger than its "normal" value.

For an interpretation of the overtone and combination bands it is necessary to take account of the rules governing the resultant species [see ref. (4)]. The relations that matter for the present analysis are summarized by the following symbolic equations:

$$a_1 \times a_1 = A_1 \quad a_1 \times a_2 = A_2 \quad a_1 \times e = E$$

$$(1) \quad e \times e = A_1 + A_2 + E, \quad (e)^2 = A_1 + E, \quad (e^3) = A_1 + A_2 + E$$

$$(e)^4 = A_1 + E + E, \quad e \times (e)^2 = A_1 + A_2 + E + E$$

$$e \times e \times e = A_1 + A_2 + E + E + E$$

To a first approximation the vibrational levels of methyl iodide can be represented by the formula

$$(2) \quad G(v_1 \dots v_6) = \sum_i \omega_i \left(v_i + \frac{d_i}{2} \right) + \sum_i \sum_{k \geq i} x_{ik} \left(v_i + \frac{d_i}{2} \right) \left(v_k + \frac{d_k}{2} \right) \\ + \sum_i \sum_{k \geq i} g_{ik} l_i l_k.$$

Here v_1, v_2, \dots, v_6 are the vibrational quantum numbers, d_i is the degree of degeneracy (1 for nondegenerate and 2 for degenerate vibrations) l_i is a quantum number of degenerate vibrations which assumes the value $v_i, v_i - 2, \dots, 1$ or 0 (it is zero for nondegenerate vibrations irrespective of the value of v_i); ω_i is the vibrational frequency (in cm. $^{-1}$) for infinitesimal

amplitudes, and x_{ik} and g_{ik} are anharmonicity constants. The last term in the energy equation is different from zero only if at least one degenerate vibration is excited. The l_i values 0, 1, 2, 3, 4 correspond to the resultant species $A_1, E, E, A_1 + A_2, E$ respectively if only one degenerate vibration is excited. Thus the states with $l_i = v_i$ in a series of overtones ($v_i = 1, 2, 3, 4, \dots$) of a

TABLE I
OBSERVED INFRARED BANDS OF METHYL IODIDE.

ν_{obs} (observed)	Type	Intensity	Assignment ¹	ν (calculated)
4088	P	15	$\nu_2 + 2\nu_5(A_1)$	4113
4109	R			
4302	\perp^2	80	$\nu_2 + \nu_4(E)$	4312
4478	\perp^3	100	$\nu_4 + \nu_5(E)$	4500
4714	P	5	$\nu_1 + \nu_2 + \nu_3(A_1)$	4755
4736	R			
4826	\perp	8	$\nu_1 + 2\nu_5(A_1)$	4730
4980	\perp	0.4	$\nu_4 + 2\nu_5(E)$	4820
5160	P	1.5	$\nu_2 + \nu_3 + \nu_4(E)$	4845
5182	R		$\nu_1 + \nu_3 + \nu_5(E)$	
5340	\perp^4	?	$\nu_3 + \nu_4 + \nu_5(E)$	5033
5450	\perp^4	?	$\nu_2 + \nu_4 + \nu_5(A_1)$	5192
5696	\perp^5	8	$\nu_4 + \nu_5 + \nu_6(A_1, E)$	5380
5837	\perp^6	>10	$\nu_1 + 2\nu_2(A_1)$	5473
5886	\perp^7	40	$4\nu_5(E)$	5722
5987	\perp^8	>10	$\nu_2 + \nu_4 + \nu_5(E)$	5752
6045	P	40	$\nu_1 + 2\nu_5(E)$	5831
6066	R		$? \nu_4 + 2\nu_5(E)$	
6125	\perp	15	$2\nu_1(A_1)$	5921
6594	$?$	0.1	$2\nu_1(A_1)$	5940
6751	\perp	0.5	$\nu_1 + \nu_4(E)$	6030
6798	P	3	$2\nu_4(A_1)$	6120
6816	R		$2\nu_4(E)$	
6975	\perp	2	$? 2\nu_4 + \nu_5(A_1, E)$	6653
7295	\perp^4	0.05	$2\nu_1 + \nu_5(E)$	6820
7357	\perp^4	0.1	$\nu_1 + \nu_4 + \nu_5(A_1)$	6910
7505	\perp^8	2	$2\nu_4 + \nu_5(E)$	7000
8036	\perp	0.05	$? \nu_2 + 2\nu_4(E)$	7372
8191	\perp	0.1	$? 2\nu_1 + \nu_5(E)$	7380
8335	P	0.1	$2\nu_4 + \nu_5(A_1, E)$	7560
8356	R		$? \nu_3 + 2\nu_4 + \nu_5(A_1, E)$	
8672	P	9	$? 2\nu_1 + \nu_5 + \nu_6(A_1, E)$	8441
8692	R		$? 2\nu_4 + \nu_5 + \nu_6(A_1, E)$	
8723	$?$	2	$? 3\nu_1(A_1)$	8910
8843	$?$	1	$? 2\nu_1 + \nu_4(E)$	9000
8880	P	3	$\nu_1 + 2\nu_4(A_1)$	9091
8902	R		$\nu_1 + 2\nu_4(E)$	
8984	\perp^9	1	$3\nu_4(E)$	9180
9122	P	0.5	$3\nu_4(A_1)$	9180
9147	R			
9552	$?$	0.5		
9816		0		
10091		0		
11347		1	$4\nu_1(A_1)$	11880

degenerate vibration have species $E, E, A_1 + A_2, E, \dots$ giving rise to a series of bands with types $\perp, \perp, //, \perp, \dots$ in this order. A striking example of such a series is found for methyl iodide (see below).

In the region of the first overtone of the C-H stretching vibration the following binary combinations must be expected.

$$2\nu_1(A_1), \quad \nu_1 + \nu_4(E), \quad 2\nu_4(A_1 + E).$$

Of these $2\nu_4$ would be expected to have the highest frequency since ν_4 is larger than ν_1 . The band of highest frequency (6125 cm^{-1}) in the group near 6000 is a \perp band and must therefore be interpreted as the E component of $2\nu_4$, the A_1 component being the $//$ band at 6055 cm^{-1} , which is the band of second highest frequency in this group. This assignment implies that g_{44} in (2) is positive (and equal to 17.5) since the A_1 and E components of $2\nu_4$ have $l_4 = 0$ and 2 respectively. The binary combinations $\nu_1 + \nu_4$ and $2\nu_1$ must be identified with the observed bands at 5987 and 5886 cm^{-1} respectively. The two remaining bands (of \perp type) at 5837 and 5696 cm^{-1} cannot be accounted for as binary combinations. However they can readily be interpreted as the E components of $\nu_1 + 2\nu_5$ and $4\nu_5$ respectively if resonance with $\nu_1 + \nu_4$ is assumed to cause their comparatively large intensity. The other components of $\nu_1 + 2\nu_5$ and $4\nu_5$ as well as the three components of $\nu_4 + 2\nu_5$ are presumably too much overlapped by the main bands or too weak to be detectable.

In the group of bands corresponding to the second overtone of the C-H stretching vibration the following ternary combinations will be expected

$$3\nu_1(A_1), \quad 2\nu_1 + \nu_4(E), \quad \nu_1 + 2\nu_4(A_1 + E), \quad 3\nu_4(E + A_1 + A_2).$$

Of these, on the basis of the interpretation of the band group near 6000 cm^{-1} , that component of $3\nu_4$ that has the highest l_4 (which is 3) should have the highest frequency. According to the previous discussion this would be a $//$ band (unlike the highest frequency band of the 6000 cm^{-1} group). It seems very significant that the observed band of highest frequency of the 9000 group is indeed a $//$ band (see Fig. 3).

Footnotes to Table I:

¹ When several substates arise (see text) only that one is indicated which can give rise to the observed band type.

² This band shows a clear intensity alternation. The spacing of successive lines is 9.4 cm^{-1} .

³ The fine structure of this band indicates overlapping by another band, possibly $\nu_4 + \nu_5 (A_1)$ or $\nu_1 + \nu_5 (E)$.

⁴ These bands are badly overlapped by the water bands.

⁵ This band shows a clear intensity alternation particularly at higher pressures than used for Fig. 1. The spacing of successive lines is approximately 8.6 cm^{-1} .

⁶ These bands are on the slopes of the stronger band 5886 . Therefore their intensities and band centers cannot be very accurately estimated.

⁷ This band is overlapped by the adjacent \perp bands. Therefore the P and R maxima cannot be definitely identified.

⁸ This band has a strong central branch (see text).

⁹ This is the band found by Verleger, probably consisting of two overlapping bands. The bands show the characteristic intensity alternation.

Because of the large number of expected ternary combinations which is considerably increased if the slight resonance of $2\nu_6$ with ν_1 or ν_4 is taken into account the remaining observed bands in the region near 9000 cm.^{-1} cannot be as uniquely assigned as those in the region near 6000 cm.^{-1} . A tentative assignment is presented in Table I. This table includes also the assignments for the bands not in the groups thus far mentioned. Those for the bands below 5500 cm.^{-1} seem to be quite definite. Also several of the bands between 6000 and 9000 cm.^{-1} seem to be uniquely identified.

The last column of Table I contains calculated frequencies on the assumption of harmonic vibrations. A determination of some of the anharmonicity constants x_{ik} and g_{ik} in (2) does not seem profitable on the basis of the present data. Work with higher dispersion, which is being planned, seems necessary for this purpose.

Acknowledgment

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COMPRESSIBILITY OF GASES AT HIGH TEMPERATURES

I. METHODS OF MEASUREMENT AND APPARATUS¹

BY W. G. SCHNEIDER

Abstract

Methods and apparatus used for compressibility measurements of gases in the temperature range 0° to 600° C. are described. A further method which can be used at temperatures above 600° C. is also described. Data for some measurements with pure helium at 0° and at 600° C. are given, from which the values (in Amagat units), 0.527×10^{-3} per atm. $\pm 0.003 \times 10^{-3}$ and 0.439×10^{-3} per atm. $\pm 0.005 \times 10^{-3}$ were obtained for the second virial coefficient at 0° and 600° C. respectively.

Introduction

A program has been undertaken in these laboratories to extend the compressibility measurements of a number of important gases to higher temperatures. The present paper deals with the methods and the apparatus developed for these measurements. As a test of the method the second virial coefficient of helium has been measured at 0° and at 600° C. A more extensive series of measurements in this temperature range is now in progress.

The methods of measurement adopted for the present purpose are based on a method first described by Burnett (3). This is an expansion method which eliminates the necessity of making volume measurements directly. For this reason it is particularly well suited for measurements at higher temperatures where volume measurements cannot be made with the same degree of precision as measurements of temperature and pressure. For our purpose it is convenient to use a somewhat different notation from that given by Burnett and also to modify the procedure for treating the data. It has also been found possible to adapt the method to a further modification which involves the heating of but one gas pipette. This latter method is particularly useful for measurements at high temperatures.

Method

Most of the permanent gases at temperatures above 0° C. and pressures below 75 atm. have either linear or parabolic isotherms, which can be accurately fitted to simple virial expressions of the form

$$P V/n = A_T + B_T P + C_T P^2 \quad (1)$$

where n is the mole number.

For hydrogen and helium the contribution of the third virial term is negligible even at 0° C. In such case the second virial coefficient can be obtained in a very simple way by Burnett's expansion method.

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Consider two pipettes at uniform temperature T connected through a pressure valve. Let the volume of the pipettes be V_I and V_{II} . Suppose n moles of gas are originally contained in pipette I at a pressure P_I and at temperature T . Then

$$P_I V_I / n = A_T + B_T P_I. \quad (2)$$

Now let the gas be expanded through the pressure valve into the second pipette, giving rise to a lower pressure P_{II} . Then, since n is unchanged,

$$\frac{P_I V_I}{A_T + B_T P_I} = \frac{P_{II}(V_I + V_{II})}{A_T + B_T P_{II}}. \quad (3)$$

Rewriting and letting P_m and P_{m+1} be any two corresponding pressures before and after expansion,

$$P_m / P_{m+1} = N + (N - 1)(B_T / A_T) P_m, \quad (4)$$

where

$$N = (V_I + V_{II}) / V_I.$$

In practice it is convenient to carry out about five or six expansions over a fairly wide range of initial pressures and plot the pressure ratio P_m / P_{m+1} against the initial pressure P_m . From the intercept and the slope of the plot the ratio B_T / A_T can be evaluated. To obtain B_T itself an additional relation is needed. Using Amagat units, there results from Equation (1) at 0°C . (for linear isotherms),

$$A_0 + B_0 = 1, \quad (5)$$

where the subscript 0 corresponds to 0°C .

Also

$$A_T = A_0 T / T_0. \quad (6)$$

Thus from a pressure ratio-pressure plot carried out for the same gas at 0°C . one can by combining (4) and (5) obtain A_0 (and of course also B_0). Then for any temperature T , B_T can be evaluated with the aid of Equation (6).

For gases giving rise to parabolic isotherms Equation (4) becomes:

$$P_m / P_{m+1} = N + (B_T / A_T)(N - 1)P_m + (C_T / A_T)(P_m N - P_{m+1})P_m. \quad (7)$$

Here N can again be obtained from the intercept of the curve, but it is preferable to measure N directly with a gas which will give a linear isotherm, such as helium; then, if N is known, (7) can be rearranged to give a linear plot as follows:

$$\frac{P_m / P_{m+1} - N}{P_m} = (N - 1)(B_T / A_T) + (C_T / A_T)(P_m N - P_{m+1}). \quad (8)$$

By plotting the left-hand side against $(P_m N - P_{m+1})$, the second and third virial coefficients can be evaluated from the intercept and the slope of the curve.

For measurements of the second virial coefficient at very high temperatures (or very low temperatures) it is more convenient from the experimental point of view to maintain one pipette at the extreme temperature and the second pipette at some convenient temperature. For some measurements at high temperatures 0°C. was selected as the temperature of the second pipette. The ice bath in which the pipette was immersed also served as the cold junction for the measuring thermocouples of the first pipette. The same general procedure as outlined above can be employed under these conditions. When the isotherms are linear, we have in place of Equation (3) above:

$$\frac{P_I V_T}{A_T + B_T P_I} = \frac{P_{II} V_T}{A_T + B_T P_{II}} + \frac{P_{II} V_0}{A_0 + B_0 P_{II}}, \quad (9)$$

where V_T is the volume of the pipette held at temperature T and V_0 the volume of that at 0°C. It is assumed that the virial coefficients at 0°C. are accurately known or can be measured by an application of Equation (4). Rearranging (9) and again letting P_m and P_{m+1} be corresponding pressures before and after expansion we obtain:

$$\begin{aligned} P_m/P_{m+1} + (B_0/A_0)(P_m - P_{m+1}) - (M-1)(B_T/A_T)^2 P_m P_{m+1} \\ = M + (M-1)(B_T/A_T)(P_m + P_{m+1}), \end{aligned}$$

where

$$M - 1 = \frac{A_T}{A_0} \frac{V_0}{V_T} = \frac{T}{T_0} (N - 1),$$

and now

$$N = \frac{V_T + V_0}{V_T}. \quad (10)$$

The third term on the left turns out to be very small and can easily be obtained by successive approximation. Hence, as before, B_T can be obtained analytically from any two sets of pressure measurements, but in order to obtain a good "smoothing" of the data it is preferable to carry out about five or six expansions (in our case covering a pressure range from 80 to 10 atm.) and plot the left-hand member of (10) against $(P_m + P_{m+1})$. The best straight line, fitted by least-squares, is drawn through the points, and from the intercept and the slope of the line B_T can be evaluated.

Apparatus

(a) Pressure Measurements

The pressure measurements were made with a free piston gauge. The gauge block was similar in design to that of Keyes (6), and permitted an oscillation of the piston through a 60° angle while measurements were being

made. The gauge was calibrated against the vapor pressure of highly purified carbon dioxide at 0°C ., as recommended by Professor Keyes. The value of the vapor pressure of carbon dioxide at 0°C . was taken to be 26144.7 International millimeters of mercury (2). At this pressure the gauge had a sensitivity of 1 in 100,000. Two pistons having areas of 0.94968 and 1.5451 cm^2 were used interchangeably. Balance of the loading on the piston was indicated by a mercury U-tube having a glass capillary in each arm so that the mercury surface could be observed at all times (see Fig. 1). At the top of each capillary was mounted an electric contact in the form of a needle; each needle was adjusted to the same height. One arm of the U-tube was connected to the piston gauge through an oil line, and the other arm to the gas to be measured. At balance an increment of 0.2 gm. on the scale pan of the gauge caused the electric needles, which were made to flash small neon bulbs, to make or break contact with the mercury in both arms of the U-tube.

A mercury injector was used to adjust the height of the mercury in the U-tube. The weights used with the gauge were calibrated by the Metrology Section of the National Research Council.

(b) Temperature Measurements

For measuring the temperatures in the range from 0° to 600°C ., a platinum resistance thermometer was used together with a Leeds and Northrup G-2 Mueller Bridge. The thermometer was of conventional design but was enclosed in a quartz jacket and had been annealed at 640°C . It also was calibrated by the Metrology Section of the National Research Council of Canada. Comparison of this thermometer with two thermometers constructed and calibrated by Leeds and Northrup (Type 8163) gave excellent agreement.

(c) The Thermostat

The thermostat consisted of a well insulated stainless steel tank equipped with a cover and two high-speed stainless steel stirrers of the type described by Beattie (1). A mixture of shaved ice and water was used in the thermostat for the 0°C . isotherms. Oil was used as the bath liquid below 200°C . and a eutectic mixture of sodium, potassium, and lithium nitrates was used in the range from 200° to 600°C . Temperature control to better than 0.01°C . was obtained by means of a stainless-steel-jacketed platinum resistance thermometer immersed in the bath and connected to a Wheatstone bridge. The bridge unbalance was measured by means of a sensitive mirror galvanometer having a 20 ft. optical lever which actuated a photocell-relay circuit.

(d) The Gas Pipette Assembly

The gas pipette assembly is illustrated in Fig. 1. The volumes of the pipettes were approximately 58 cc. for the first and larger pipette and 28 cc. for the second pipette. This ratio of volumes gave a convenient spacing of the experimental points on a plot of pressure ratio vs. pressure. The pipettes

were made of stainless steel with a wall thickness of 3 mm. All joints were welded. Each pipette was surrounded by a stainless steel pressure jacket having a 1 cm. wall thickness and joined to a stainless steel capillary by

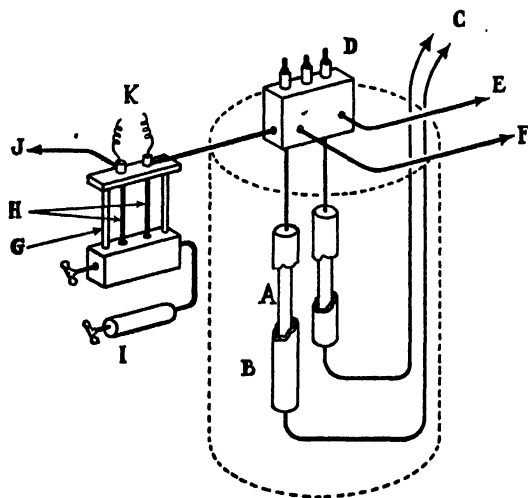


FIG. 1. Gas pipette assembly.

- A — gas pipettes*
- B — pressure vessels surrounding gas pipettes*
- C — gas connections for B*
- D — expansion valve block*
- E — vacuum line*
- F — line to compressor and gas supply*
- G — mercury U-tube*
- H — glass capillaries*
- I — mercury injector*
- J — pressure gauge connection*
- K — electric needle contact leads*

means of which a gas pressure (either helium or nitrogen) could be applied on the outside wall of the gas pipette to equalize the pressure within the pipette. By this means change of volume of the gas pipettes with pressure was minimized. It should be noted that volume changes of the pipette due to changes in temperature will not directly affect the results since the volume-ratio of the pipettes is obtained for each isotherm from the intercept of the pressure ratio - pressure plot.

The pipettes were connected by means of stainless steel capillary (0.6 mm. bore) to the expansion needle valve mounted on the thermostat cover. The expansion valve block, which was water-cooled, also contained two shutoff needle valves, one leading to a vacuum line, the other to a gas supply line from the gas compressor. The expansion valve (shown in Fig. 2) was designed to keep the gas volume within the valve block small, both before and after opening the valve. "Teflon" packing was used for all pressure valves.

The expansion valve block was connected to the mercury U-tube by means of a 0.4 mm. bore capillary. This together with the small volume in the expansion valve block formed the "dead" space or unheated volume of the

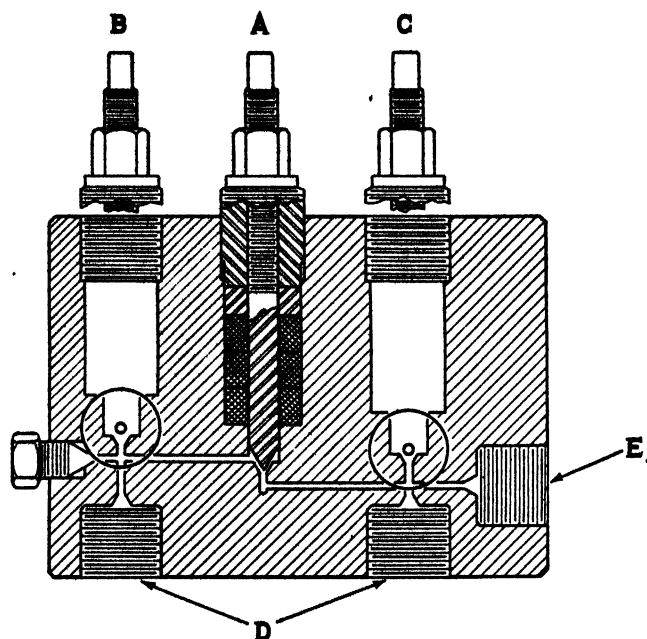


FIG. 2. *Expansion valve block.*

- A — expansion valve*
- B — valve to vacuum line*
- C — valve to compressor*
- D — gas pipette connections*
- E — connection to mercury U-tube*

assembly and had to be corrected for; it comprised about 0.5% of the total volume of the pipette assembly. Actually this percentage could conveniently have been reduced further by using larger pipettes, but since it was our purpose initially to develop a method which could be used at even higher temperatures, where a platinum pipette heated by an electric furnace would be required, a pipette of larger size appeared impractical.

Procedure

The gas to be measured was compressed by means of a mercury piston in a large pressure bomb and then forced into the large pipette to a pressure of 75 to 80 atm. At the same time the pressure was built up in the pressure vessel surrounding the pipette and thereafter the pressure inside and outside the pipette were kept balanced to within 1 atm. When temperature and pressure equilibrium had been obtained the pressure was recorded, and the gas was expanded into the second pipette. After the pressure was again measured, the expansion valve was closed and the gas in the small pipette was

allowed to expand into a gasometer. After evacuating the small pipette, the above cycle was repeated. In this manner about six pressure ratios were obtained. It was then convenient to repeat the isotherm, starting at a lower initial pressure so as to stagger the points on the pressure ratio - pressure plot.

Corrections and Treatment of Data

The pressures measured by the piston gauge directly were corrected for barometric pressure, for variation in temperature of the piston, and for the contribution to the pressure due to the difference in level of the oil at the bottom of the piston and at the top of the mercury in the U-tube. Correction was also made for the air buoyancy of the weights used with the piston gauge.

Since there was a small volume of gas contained in the expansion valve and in the capillary leading to the mercury U-tube which was not in general at the temperature of the thermostat, a small correction had to be applied to the measured pressure. For this purpose the total unheated space was divided into two regions, the one comprising the volume within the valve block, the other the volume of the capillary connecting the mercury U-tube. The mean temperature of each region was recorded during the course of the pressure measurements, and the volume of each region was determined separately by a gas expansion method described by Kaminsky and Blaisdell (5).

It was found that in order to achieve an accuracy of 1% in the measurements of the second virial of helium at 600° C. by the above method, considerable care had to be exercised in making the unheated-volume correction; at lower temperatures the accuracy is better. With the present apparatus, use of the perfect gas law instead of Equation (2) to correct for the unheated space would cause an error of 3% in the slope of the pressure ratio - pressure plot for the 600° C. isotherm; for the 0° C. isotherm the difference is negligible. The general correction factors derived for these cases are given in Appendix I.

The corrected pressure ratios were then plotted against the corrected pressures. The best straight line through the points was obtained by a least-squares fit. In doing this it is desirable to weight the higher pressure points more than the lower pressure points since the relative precision with which the higher pressure can be measured is greater. A satisfactory method appears to be that of weighting each point in direct proportion to the absolute value of the pressure as shown on the abscissa. The values of the intercept and slope obtained from the weighted least-squares fit are then used to calculate the second virial coefficient (and also the third virial coefficient where Equation (8) above is applicable).

Results and Estimate of Errors

Table I shows a typical set of results obtained for pure helium with both gas pipettes maintained at a temperature of 0° C. The corresponding pressure ratio - pressure plot is shown in Fig. 3. Two series of expansions were carried out; six expansions were made in the first series, and five in the second. The

TABLE I

EXPANSION DATA FOR HELIUM AT 0° C. AND AT 600° C. WITH BOTH PIPETTES AT THE SAME TEMPERATURE

Temp., °C.	Expansion	Pressure, atm.	Pressure ratio (P_m/P_{m+1})	Weight		
0	Series I					
	1	P_0 P_1	76.5380 50.8196	1.506071	76.5	
	2	P_1' P_2	50.8187 33.8877	1.499618	50.8	
	3	P_2' P_3	33.8869 22.6630	1.495257	33.9	
	4	P_3' P_4	22.6629 15.1873	1.492231	22.7	
	5	P_4' P_5	15.1874 10.1892	1.490543	15.2	
	6	P_5' P_6	10.1896 6.8437	1.488908	10.2	
	Series II					
	1	P_0 P_1	66.1948 44.0282	1.503462	66.2	
	2	P_1' P_2	44.0266 29.3932	1.497851	44.0	
	3	P_2' P_3	29.3929 19.6742	1.493981	29.4	
	4	P_3' P_4	19.6730 13.1901	1.491499	19.7	
	5	P_4' P_5	13.1899 8.8536	1.489778	13.2	
	600	Series I				
		1		80.6624 54.0291	1.492943	80.7
		2		54.1015 36.2829	1.491103	54.1
3			36.3318 24.3836	1.490007	36.3	
4			24.4149 16.3964	1.489043	24.4	
5			16.4178 11.0284	1.488681	16.4	
6			11.0432 7.4202	1.488260	11.0	

TABLE I—*Concluded*

EXPANSION DATA FOR HELIUM AT 0° C. AND AT 600° C. WITH BOTH PIPETTES AT THE SAME TEMPERATURE—*Concluded*

Temp., °C.	Expansion	Pressure, atm.	Pressure ratio (P_m/P_{m+1})	Weight
600	Series II			
	1	67.0778 44.9586	1.491991	67.1
	2	45.0184 30.2035	1.490505	45.0
	3	30.2433 20.3025	1.489634	30.2
	4	20.3296 13.6534	1.488978	20.3
	5	13.6722 9.1857	1.488424	13.7

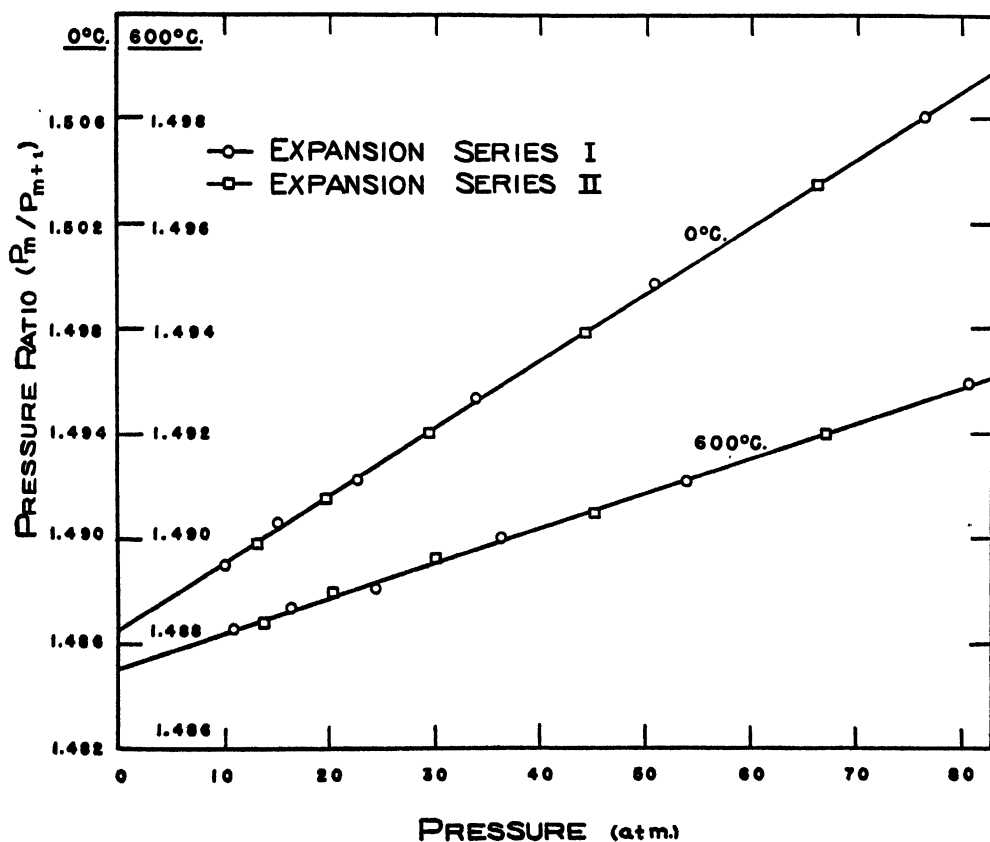


FIG. 3. Plot of pressure ratios against pressure for helium at 0° C. and at 600° C.

pressure after any one expansion, say P_1 , differed slightly from the initial pressure to be used for the next expansion (indicated by a prime), in this case P'_1 , due to a slight volume change occasioned by the closing of the expansion valve. Hence in each case it was necessary to remeasure the pressure after the expansion valve was closed, and to use this value of the pressure together with that obtained after the valve was subsequently opened, in order to obtain the correct pressure ratio.

A least-squares fit to the weighted points gives for the 0° C. pressure ratio – pressure plot

$$P_m/P_{m+1} = 1.487600 + 0.256365 \times 10^{-3} P_m,$$

with a probable error of the slope equal to $0.775 \times 10^{-6} \text{ atm.}^{-1}$, and a probable error for the intercept of 40.5×10^{-6} . This leads to a precision of the second virial when evaluated from the plot of Fig. 3, of 1/330. The over-all possible error, taking into account all errors and corrections, is somewhat greater than this and is estimated for the 0° C. measurements to be approximately 0.5%. The values of the first and second virial coefficients at 0° C. obtained from the above values of the intercept and slope with the aid of Equation (5), are, in Amagat units:

$$A_0 = 0.999473;$$

$$B_0 = 0.527 \times 10^{-3} \text{ per atm.}$$

For comparison, the value of the second virial coefficient of pure helium at 0° C. given by Holborn and Otto (4) is $0.524 \times 10^{-3} \text{ per atm.}$

Similar series of measurements with both pipettes at 600° C. are also given in Table I and the corresponding plot is also shown in Fig. 3. The ordinates in this case are plotted on twice as large a scale as was used for the 0° C. plot. The intercepts for the two plots are slightly different owing to an alteration in the pipette assembly which changed the volume ratio. The value of the second virial coefficient at 600° C., evaluated from the plot by least-squares, is in Amagat units $0.437 \times 10^{-3} \text{ per atm.}$ No values at this temperature were found in the literature for comparison. The over-all error in the measurement at 600° C. is estimated to be about 1%. This error could be reduced somewhat however by employing larger gas pipettes. A series of measurements of the second virial coefficient of helium in the temperature range 0° to 600° C. at 100 degree intervals, employing the method illustrated by Fig. 3, is now in progress.

Table II contains data for two series of expansions obtained with one pipette maintained at 600° C. and the second pipette at 0° C. Fig. 4 shows the corresponding plot for these measurements, where the ordinate $G(P_m, P_{m+1})$ is the left-hand side of Equation (10). To evaluate the ordinates a plot

TABLE II

EXPANSION DATA FOR HELIUM AT 600° C. WITH THE SECOND PIPETTE AT 0° C.

Expansion	Pressure, atm.	$\frac{P_m/P_{m+1} + (B_0/A_0)(P_m - P_{m+1})}{(M - 1)(B_T/A_T)^2 P_m P_{m+1}} -$	$P_m + P_{m+1},$ atm.	Weight
Series I				
1	82.6670 1.5473	1.619951	134.2123	134.2
2	51.7924 32.2574	1.615830	84.0498	84.0
3	32.4102 20.1714	1.613153	52.5817	52.6
4	20.2665 12.6060	1.611701	32.726	32.9
5	12.6662 7.8779	1.610334	20.5441	20.5
Series II				
1	70.0769 43.6730	1.618401	113.7499	113.7
2	43.8801 27.3233	1.614629	71.2034	71.2
3	27.4523 17.0830	1.612433	44.5353	44.5
4	17.1642 10.6763	1.611099	27.8405	27.8
5	10.7271 6.6703	1.610314	17.3975	17.4

was first made neglecting the third term on the left of Equation (10). From this plot a preliminary value of B_{600} was obtained, which was then used for the first approximation in an iteration procedure to evaluate the quadratic term in Equation (10). The final curve, shown in Fig. 4, was fitted by least squares with the result:

$$G(P_m, P_{m+1}) = 1.608761 + 0.838337 \times 10^{-4}(P_m + P_{m+1}).$$

From the values of the slope and intercept we obtain for the second virial coefficient at 600° C. (again in Amagat units), $B_{600} = 0.440 \times 10^{-3}$ per atm., in good agreement with the value obtained with both pipettes at the same temperature. The present method, whereby one pipette can be heated in a furnace and the other immersed in an ice bath, is now being employed for further measurements of the second virial coefficient of helium at 600° C. and above.

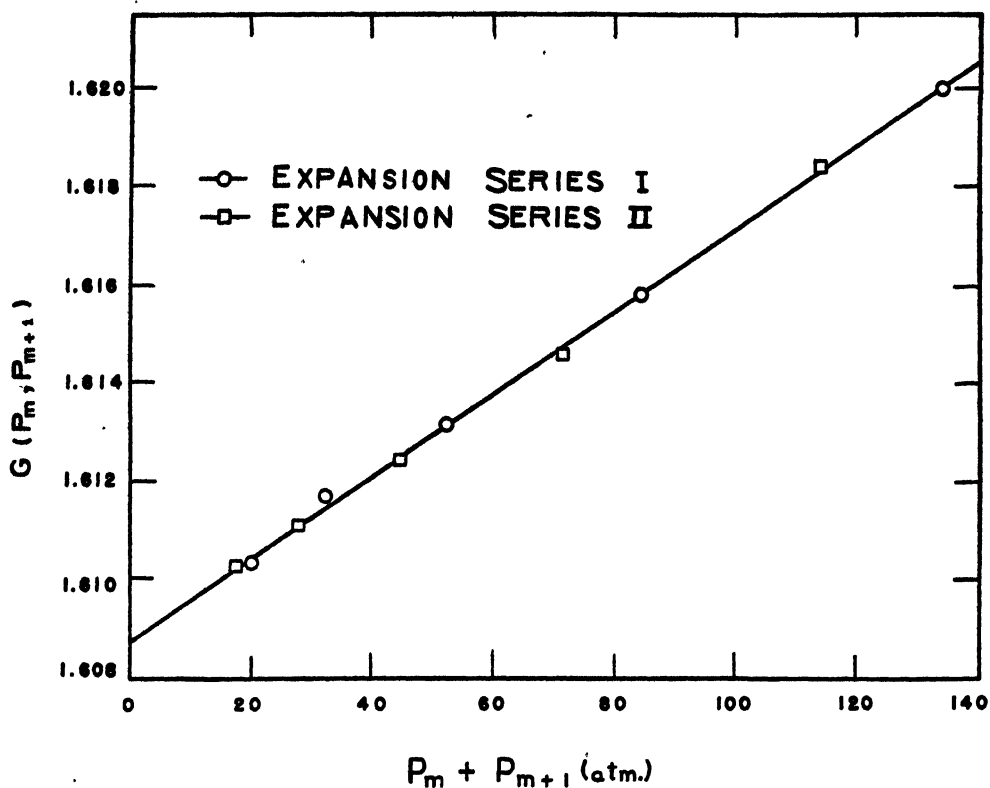


FIG. 4. Plot of Equation (10) for helium with one pipette at 600° C. and the second pipette at 0° C.

Acknowledgment

I wish to acknowledge the assistance of Mr. W. A. Stevenson in the construction and testing of the apparatus and the assistance of Dr. Norman Hollies in the early stages of this work. We are indebted to Prof. F. G. Keyes of the Massachusetts Institute of Technology for helpful discussion in connection with this work and for supplying us with blueprints for the pressure gauge.

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APPENDIX I

Correction to the Measured Pressures of the Two-Pipette Compressibility Apparatus Due to Small Unheated Gas Volumes

Suppose the two pipettes at the one temperature.

Let P_e be the measured pressure and P_f the corrected pressure which the gas would have if the total volume of gas were at a temperature T , then

$$P_f = FP_e, \quad (1)$$

where F is a correction factor. To evaluate F we consider a mass of gas contained at a pressure P_e in a volume subdivided into several regions v_i each at a different temperature t_i . If V is the total volume,

$$\sum v_i = V. \quad (2)$$

We shall consider two cases:

Case 1

When the temperatures t_i are not very different (less than 100 degrees) from the temperature of the pipettes, T , the perfect gas law equation is sufficiently accurate to compute F . Then we may write

$$\frac{P_f \sum v_i}{T} = P_e \sum \left(\frac{v}{t} \right)_i, \quad (3)$$

where the summation extends to all volume regions of different temperature, including the pipette volume, at temperature T . Thus,

$$F = \frac{T \sum \left(\frac{v}{t} \right)_i}{V}. \quad (4)$$

Case 2

When the temperature of the unheated space is quite different from that of the pipettes, a more refined correction than that given by (4) is necessary. For this purpose we use instead of the perfect gas law:

$$PV = nRT\psi(P) \quad (5)$$

where n is the mole number and R the gas constant, and where, for the case of the virial law $PV/n = A_T + B_TP$,

$$\psi(P) = (1 + B'P), \quad (6)$$

B' being B_T/A_T . Then Equation (3) becomes:

$$\frac{P_f \sum v_i}{T\psi_T(P_f)} = P_e \sum \left(\frac{v}{t\psi_t(P_e)} \right)_i. \quad (7)$$

Substituting from (1) for P_f , using (6), and letting

$$S = \Sigma \left(\frac{v}{t \psi_t(P_s)} \right)_t, \quad (8)$$

we obtain

$$F = \frac{ST}{V - STB'_T P_s}. \quad (9)$$

It is assumed here that the boundaries of each volume region are sharply defined and that the temperature is uniform throughout each region. Actually in practice there is a temperature gradient near the boundary of each volume region and in applying (4) or (9) a mean temperature for each region is used. The error introduced by this approximation depends on the experimental arrangement, and with care can be made negligible.

There will be a correction factor of the type given by (4) or (9) before expansion of the gas, involving only the volume of the first pipette and its associated unheated space; and a second factor, after the gas is expanded, which involves the volumes of both pipettes and their associated unheated volumes.

Also for (9) a knowledge of B' at each of the temperatures t_i is required to evaluate F .

For routine computation (9) can be expanded in a power series in the pressure P_s , and to a sufficiently good approximation (in the temperature range 0° to 600° C.) is given by:

$$F = F_0(1 - \alpha P_s), \quad (10)$$

where F_0 is the correction factor (assuming an ideal gas law) given by Equation (4), and α is a coefficient which can be evaluated by computing F by Equation (9) for a single measured pressure P_s . Then for all other measured pressures (assuming the "dead"-space volumes and temperatures to remain constant), the correction factor can be obtained from (10).

In the case for which the two pipettes are at different temperatures, similar treatment yields a quadratic equation whose solution is the correction factor F . Again, however, Equation (10) can be used.

USE OF THE CATHODE RAY OSCILLOGRAPH IN THE MEASUREMENT OF METAL AREAS AND THE KINETICS OF ELECTRODE REACTIONS¹

A. T. HUTCHEON² AND C. A. WINKLER

Abstract

A commercial type cathode ray oscillograph has been used in conjunction with three stages of direct current amplification to give suitable voltage amplification in the range 0.001 to 1 v. The effect of traces of grease in diminishing the measured surface area of silver amalgam has been observed. Curves are shown for the determination of cadmium surface areas and rate of increase of cadmium polarization.

Introduction

The instrument to be described in this paper was developed to obtain information on the change in surface area during cadmium deposition, with a view to finding "true current density" – polarization relations. The advantages of the cathode ray oscillograph (C.R.O.) for measuring the rate of electrode potential increase were early recognized by Newbery (8) and it has been used consistently by him since that time (6, 9).

In principle, the C.R.O. is utilized by suitably amplifying the potential between the electrode under observation and a reference electrode, and applying the amplified potential to the Y-axis plates of the C.R.O. A trace of potential *vs.* time is made on the screen. The size of the trace is conveniently controlled by adjustment of the sweep velocity and the electrolyzing current (or amplification).

In the measurement of the rate of electrode potential increase, the following characteristics are desirable in the measuring instrument (6).

- (a) Ability to operate on minimum power in order that negligible current be drawn from the cell under observation i.e., high input impedance.
- (b) Rapid response to potential change since many electrode potentials are established in a fraction of a second, i.e., negligible inertia.
- (c) Variable sensitivity control to cover a broad range of potentials.
- (d) Variable sweep frequency, as low as 1 c.p.s..
- (e) Automatic recording of the time and potential.

The negligible capacity and broad frequency range adjustments of the new types (Du Mont 208-B) of C.R.O. make them particularly suitable for conditions (b) and (d). To obtain high sensitivity, the C. R. O. must be used in conjunction with a direct current amplifier. Progress in electronics has made the difficulties attending d-c. amplification somewhat less formidable, and,

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granting amplifier stability, the C.R.O. is superior to the Einthoven galvanometer (1) or the moving coil oscillograph (2, 3-5) in rapidity of response and versatility.

Experimental

A. DESCRIPTION OF APPARATUS

Some modifications in the commercial type 208-B Du Mont C.R.O. were necessary. The vertical or *Y*-axis a-c. amplifier was replaced by a d-c. amplifier. A single sweep circuit was added to control the *X*-axis and, in conjunction with this, a time-delay relay circuit to switch current on to the electrolysis cell after the spot had begun its traverse. A diagram of the complete circuit, excluding that of the C.R.O. itself, is shown in Fig. 1.

(a) *Input Circuit*

The particular design adopted for this circuit was necessary to reduce to a minimum a troublesome switching transient, which revealed itself by drastic deflections of the spot when the electrolyzing current was turned on. This transient was attributed to current leaks to ground and stray capacities to ground in the input circuit. All parts of the input circuit were insulated from ground by blocks of paraffin and placed at a distance of at least 8 in. from a grounded shield which completely enclosed the input circuit, the electrolysis cell, and the first two stages of amplification. With the resistances symmetrically placed with respect to the cell, this transient could be almost completely eliminated by adjusting R_5 and R_6 . A 90 v. dry cell battery B_1 supplied the electrolyzing current through variable resistances R_{1-6} , totalling 108 megohms.

The current to the cell was measured by determining the potential drop across a known resistance (R_7 , R_8 , or R_9) with a Leeds and Northrup potentiometer. The same potentiometer was used to measure the cathode-calomel potential and in the calibration of the *Y*-axis amplification. This calibration was made by impressing a suitable voltage from the bias battery B_2 directly on the amplifier input, photographing the deflection so produced, and measuring the voltage applied with the potentiometer. Battery B_2 was primarily included to oppose the cathode-calomel voltage and thus reduce the 'zero-electrolyzing-current' signal to the amplifiers. It also served to reduce the current flowing in the cathode-calomel circuit, although this was already negligible with an amplifier input resistance of 10^7 ohms.

(b) *D-c. Amplifiers*

Three stages of amplification covered the potential ranges:

1.0 to 0.1 v.	Stage 3
0.1 to 0.01 v.	Stages 1 + 2
0.01 to 0.001 v.	Stages 1 + 2 + 3

In each, the ground point was the cathodes of Stage 3, and the chassis or "ground" of the C.R.O. was about 60 v. positive to ground potential to give proper focusing of the spot. Stage 3 was powered from the 110 v. a-c. main

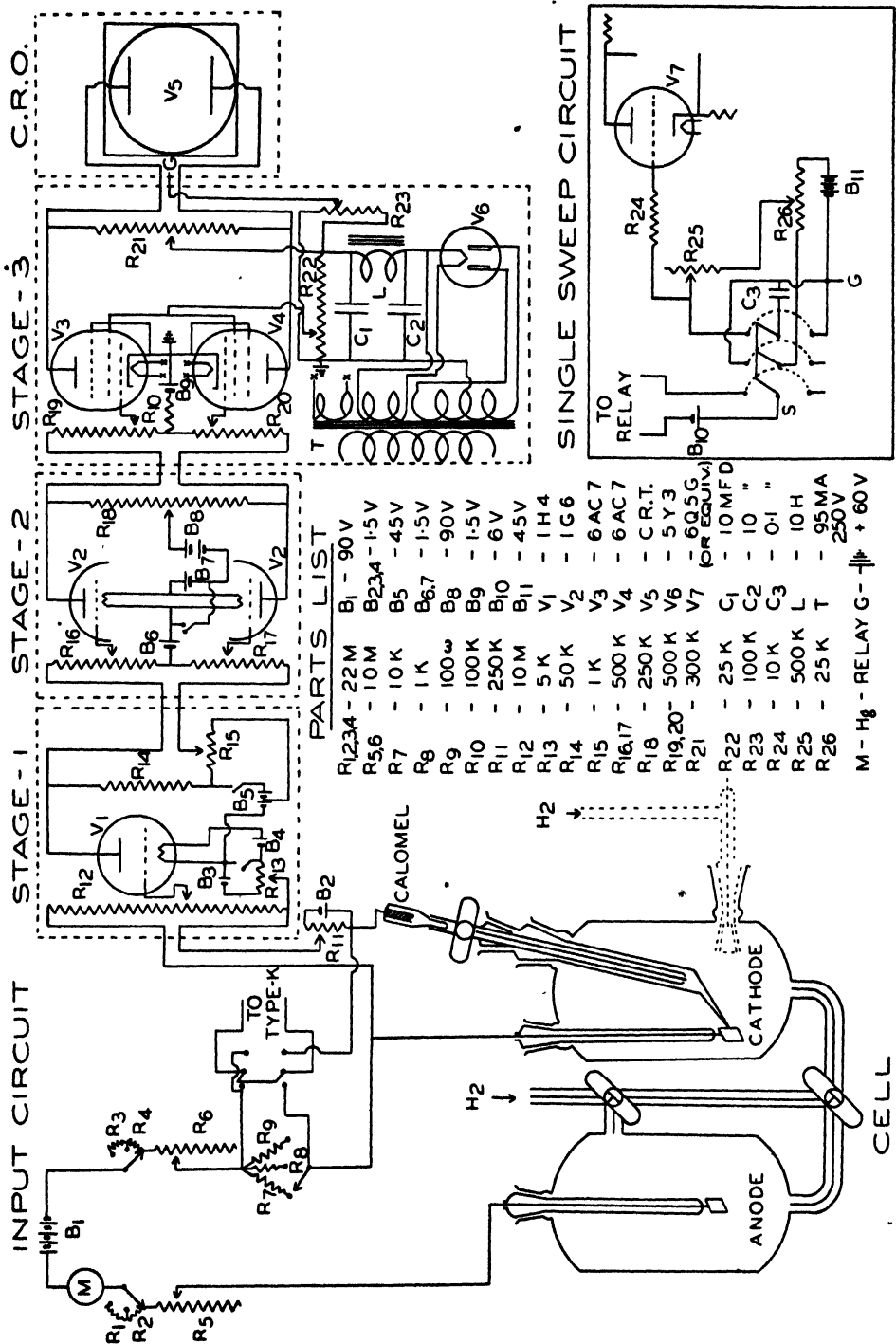
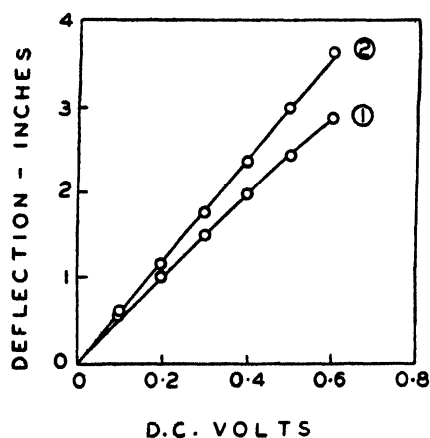


Fig. 1.

through a Sola voltage regulator. Stages 1 and 2 operated on dry cell batteries to avoid a-c. pickup and voltage fluctuations (in the main voltage line) in the early stages of amplification and to avoid the difficulties in direct coupling two a-c. operated stages. The input resistance was 10^6 ohms for stage 3 and 10^7 for Stage 1. The advantages of the "push-pull" arrangement for stability are well known (7), and the amplifiers gave good square wave response to a d-c. signal from a noncapacitive, noninductive test circuit.

Y-axis calibrations of Stage 3 and of Stages 1 + 3 are given in Fig. 2 to illustrate the degree of linearity. Calibration was made on each film to safeguard against any minor variations in the setting of the amplification controls, R_{12} , $R_{16,17}$, $R_{19,20}$.



CURVE ① - STAGE 1
CURVE ② - STAGES 1 + 3

FIG. 2.

(c) Single Sweep Circuit

Since a photograph was to be taken of the trace on the curved cathode ray tube screen, it was necessary to be able to position the potential build-up curve in the center where the curvature error would be a minimum. This was accomplished by using a combined single sweep and switching control as shown in Fig. 1. The grid of the thyratron 6Q5G in the X-axis circuit was biased to "cutoff" by charging the condenser C_3 through the variable resistor R_{25} when switch S was turned on. By suitable adjustment of R_{25} and C_3 , the thyratron was made to "fire" once and give a single sweep. When switch S was off, C_3 was "grounded" to the chassis potential. S was a triple-pole double-throw switch to which was also connected the battery circuit. By adjusting the spring tension on the mercury relay, the electrolyzing current was turned on at the correct interval after the sweep had started.

(d) Cell

The cell, Fig. 1, was of the same general design as that of Bowden and Rideal (1). It was of Pyrex, with two 400 cc. bulbs joined by a capillary through a

three-way stopcock. A second three-way stopcock permitted hydrogen to be bubbled through the solution in each half of the cell or to be passed over the solution. The capillary minimized diffusion of oxygen from anode to cathode compartments. All electrodes were sealed into ground glass joints so that the solution could be boiled under reduced pressure and hydrogen admitted without allowing air to enter the system. Contact was made between the calomel electrode and the solution through a closed stopcock wetted with solution and a fine capillary wetted with electrolyte ($N/5$ sulphuric acid).

B. PROCEDURE

The procedure was essentially that outlined by Bowden and Rideal (1). Impurities and oxygen were eliminated from the system as completely as possible and then a clean, freshly prepared electrode was immersed in the solution.

Preparation

(1) Hydrogen

Electrolytic tank hydrogen was freed from oxygen by passing it through a silica tube, 60 cm. long and 2 cm. diameter, packed with silica chips and maintained at a temperature of 900° to 1000° C. The hydrogen finally passed through a potassium hydroxide bubbler before reaching the cell.

(2) Water

Distilled water was redistilled in a silica still and stored in silica vessels. The conductivity of the water was in every case less than 2.5×10^{-6} mho.

(3) Sulphuric Acid

Merck reagent grade sulphuric was redistilled in a silica still. Spectrographic analysis failed to show traces of metals.

(4) Cadmium Sulphate

Reagent grade cadmium sulphate was twice recrystallized from redistilled water.

(5) Cathode

Where silver amalgam was the cathode, a pure silver strip, 2 cm.² in area, was freed of oxide and dissolved oxygen by heating at 300° C. in an atmosphere of nitrogen. The mercury was freshly distilled and stored under concentrated sulphuric acid before use. Both silver and mercury ultimately had to be exposed to air before immersion but the exposure was kept to a minimum by covering the silver with mercury in a nitrogen atmosphere and by having a film of concentrated sulphuric acid over the mercury while the process of rubbing the mercury into the silver, with another strip of silver, proceeded. For experiments in which grease was not excluded, one side of the amalgamated strip was covered with paraffin.

In experiments with cadmium, spectroscopically pure metal (99.99+%), machined to fit a standard tapered Pyrex joint, was freshly cut with a bottoming tool in an atmosphere of hydrogen and immediately immersed in oxygen-free electrolyte. A slight hydrogen pressure in excess of the static pressure head of solution was maintained behind the electrode. Prior to the preparation of the cathode, $N/5$ sulphuric acid was placed in the cell and degassed under reduced pressure for 12 hr. Hydrogen was then bubbled through the solution for an additional 12 hr. and the freshly prepared cathode was immersed. In some experiments, a negative potential was applied to the cathode during immersion and the solution electrolyzed for some time before measurements were taken. That this appears to remove oxygen (10) has been confirmed in the present experiments. The stopcock between the anode and cathode chambers was kept closed in grease-free experiments, since the film of solution with which it was wetted was sufficient to conduct the small currents used. This assured negligible diffusion of oxygen to the cathode chamber.

The potential build-up curves were in no instance linear immediately after the electrode had been immersed. It was assumed that traces of oxygen were still present in the solution; electrolysis for 10 or 15 min. or additional bubbling with hydrogen usually permitted linear curves to be obtained. The importance of removing oxygen cannot be overemphasized.

The photographic procedure was to expose the screen, then the overvoltage build-up curve, followed immediately by calibration of the X -axis with a 60 cycle a-c. signal and the Y -axis with a known voltage, i.e., there were four separate exposures on the same film.

Results

As an illustration of the use of the apparatus in the three voltage ranges, results are presented for the rate of increase of hydrogen overvoltage on silver amalgam and on cadmium, and of the rate of increase of polarization at a cadmium electrode in 1 N cadmium sulphate solution. All experiments were made at a room temperature of about 24° C.

A. Surface Area of Silver Amalgam—Stage 3 of Amplification

(a) With Paraffin and Grease in the System.

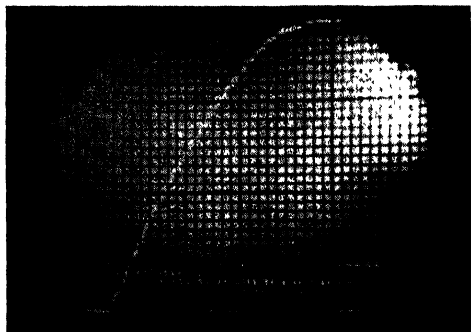
Film 1, Plate I, shows the rate of increase of hydrogen overvoltage on silver amalgam in $N/5$ sulphuric acid at 24° C. The apparent current density was 2.5×10^{-8} amp. per cm.², the Y -axis amplification 0.25 v. per in., and the X -axis calibration, 0.23 sec. per in. Taking the slope from Film 1 for $X : Y$ as 1 : 2, the value of Γ^* can be calculated as:

$$\Gamma = \frac{2 \times 10^{-8} \times 0.23}{2 \times 2.5} = 9.2 \times 10^{-7} \text{ coulomb per cm.}^2 \text{ per 100 mv.}$$

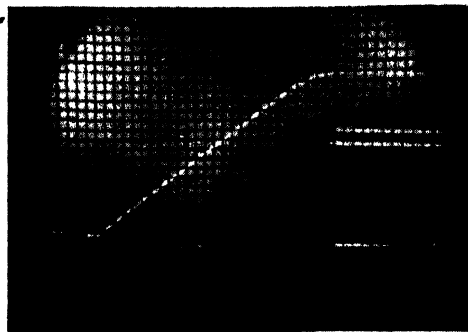
Bowden and Rideal give an average value of 6.7×10^{-7} for Γ .

* Γ is the amount of charge in coulombs necessary to cause an increase in overvoltage of 100 mv. for each apparent square centimeter of surface. $\Gamma \times 10^6$ gives the capacity in microfarads. See reference (1).

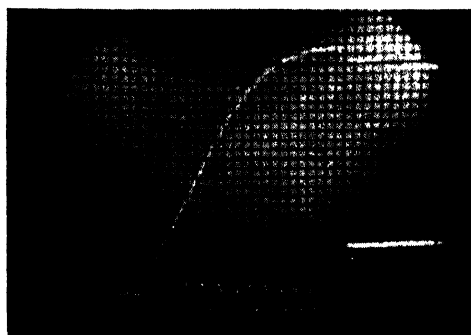
PLATE I



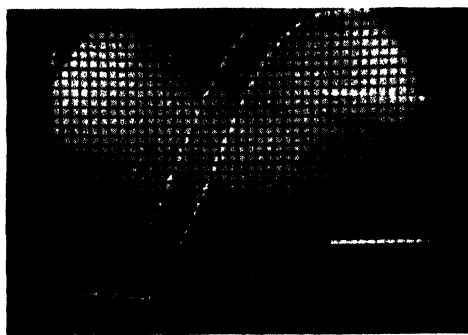
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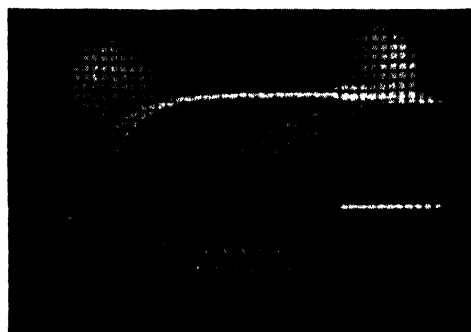
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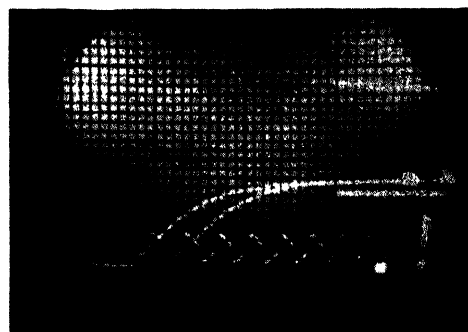
3



4



5



6

FILMS 1 to 6.

(b) *Grease-free Conditions*

With a Y -axis amplification of 0.41 v. per in. Film 2 was obtained, from which Γ may be calculated to have the value 16×10^{-7} coulomb per cm.^2 per 100 mv. This is somewhat lower than the value of $20 \mu\text{f.}$ per cm.^2 obtained by electrocapillary maximum data and by direct measurement of the capacity of the double layer by a capacitance bridge, by Proskurnin and Frumkin (10). However, it is in much better agreement than the results in which grease was not eliminated. The result is probably low owing to difficulties in avoiding contamination of the amalgam during its preparation, since it was not convenient to use a mercury cup (10) to obtain a very clean surface.

B. *Surface Area of Cadmium—Stages 1 + 3 of Amplification*

(a) The Y -axis amplification was 0.042 v. per in. for Film 3. Pure metallic cadmium was filed with a tool steel file and immersed in $N/5$ sulphuric acid. From Film 3, the value of Γ is calculated to be 120×10^{-7} coulomb per apparent cm.^2 per 100 mv. This corresponds to an accessible area six times planar, on the assumption that $\Gamma = 20 \times 10^{-7}$ for a plane surface.

(b) For Film 4, the Y -axis amplification was 0.046 v. per in. The cadmium cathode was freshly cut with a sharp steel bottoming tool and immersed in $N/5$ sulphuric acid. Calculation yields a value of 40×10^{-7} coulomb per apparent cm.^2 per 100 mv. for Γ , and an accessible area to hydrogen of twice planar.

C. *Cadmium Polarization—Stages 1 + 2 + 3 of Amplification*

Films 5 and 6 show the rate of increase of cadmium polarization when the current densities were 5.5×10^{-5} amp. per apparent cm.^2 respectively in a solution of 1 N cadmium sulphate, $N/10$ sulphuric acid, in which were immersed a cadmium cathode and cadmium anode. The Y -axis amplification was 3 mv. per in. in each film and the X -axis calibration 0.1 sec. per in. in Film 5 and 0.05 sec. per in. in Film 6.

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NATURAL VARIATIONS IN THE ISOTOPIC CONTENT OF SULPHUR AND THEIR SIGNIFICANCE¹

BY H. G. THODE, J. MACNAMARA, AND C. B. COLLINS²

Abstract

Mass spectrometer abundance measurements made on the isotopes of sulphur for samples obtained from a wide variety of sources show considerable variations. The isotopic ratios S^{33}/S^{32} and S^{33}/S^{34} were found to vary by as much as 2.5 and 5% respectively. This would mean a corresponding variation of 10% in the S^{33}/S^{36} ratio. Variations in the S^{33}/S^{34} ratio were determined with a precision of $\pm 0.05\%$. In general, sulphates whether present as gypsum deposits or in solution were found to be enriched in the heavier isotopes of sulphur. On the other hand, the hydrogen sulphide of sulphuretted well waters was usually low in these isotopes even though present in the same solutions with the sulphates. These variations are in the direction expected from theoretical considerations. A correlation between crystallization temperature of pyrites and isotopic content has been found for crystals removed from the same specimen. However, no correlation was found between crystallization temperature or geological age and isotopic content for pyrite samples collected from different geographical locations. The results indicate that the changes in the isotopic content of sulphur that occur are related to the differences in chemical properties of isotopic sulphur compounds.

Investigations of the sulphur isotopes have revealed for the first time relatively large variations in their abundances depending on the source of sulphur. Numerous samples have been studied to determine as much as possible the meaning of these variations. Details of these investigations are discussed in this paper.

In 1927, Aston (1) showed that sulphur was a mixture of isotopes consisting of S^{32} , S^{33} , and S^{34} present in abundances roughly proportional to the numbers 96, 1, and 3 respectively. Later, A. O. Nier (7) (1938) announced the discovery of S^{36} and gave abundance data for the sulphur isotopes believed to be good to 2%. Results reported in this paper show that these abundances vary from sample to sample by as much as 5% for S^{34} and 10% for S^{36} , depending on the origin of the sample.

Urey and Greiff (18) were the first to show from theoretical considerations that the isotopes of the light elements hydrogen, lithium, boron, carbon, nitrogen, and oxygen did differ slightly in their chemical properties. Their calculation of exchange constants for isotopic reactions showed that slight fractionation of these isotopes could occur in nature and in the laboratory. The energy, entropy, and free energy of substances depend on the vibrational frequencies of molecules and these depend on the masses of the atoms. Equilibrium constants for isotopic reactions can therefore be calculated by the well known methods of statistical mechanics. H. C. Urey (17) has recently made a comprehensive study of many possible isotope exchange

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reactions involving the light elements. These investigations did not include the isotopes of sulphur, for which calculations are now underway in this laboratory.

The early predictions of Urey and Greiff (18) that slight fractionation of the light element isotopes can be expected has been verified many times. Dole (3, 4) and his coworkers made extensive investigations of the isotopic content of oxygen in samples of water, air, and minerals. Their results, which were obtained by a very sensitive density method, indicated up to 3% variations in the abundances of the oxygen isotopes. Similar variations have been reported for the carbon isotopes by Nier and Gulbransen (8), and Nier and Murphy (9). Their results indicate a high C^{13} content in limestone rock and other inorganic sources and a low C^{13} content in carbon of vegetable origin.

In spite of these variations found, the view still prevails that the abundances of isotopes are remarkably constant in nature. This is perhaps due to the fact that the small variations (1 to 4%) in the isotopic content of the comparatively rare isotopes C^{13} , N^{15} , and O^{18} have little effect on the properties of the isotopic mixtures and also to the fact that these variations have been associated with only a few of the light elements. Recent work, however, shows that these variations in the isotopic abundances of elements are larger and more widespread than previously thought. Thode, Macnamara, Lossing, and Collins (15) have reported variations up to 3.5% in the abundances of the boron isotopes B^{10} and B^{11} in samples from different geological sources. Finally, the work of this paper shows that there are considerable variations in the abundances of the sulphur isotopes. It is reasonable to expect, therefore, that variations will be found in the abundances of isotopes of many of the elements well up in the periodic table.

Experimental

Preparation of Samples

The sulphur dioxide samples used in the mass spectrometer investigations are prepared by standard methods. Large enough samples of native sulphur, iron sulphide, and lead sulphide are burned in a stream of oxygen to produce about 10 cc. of sulphur dioxide at N.T.P. One cylinder of oxygen was set aside to prepare all the sulphur dioxide samples. The oxygen is passed through activated charcoal at dry-ice temperature and concentrated sulphuric acid to remove moisture and hydrocarbon impurities. Any water of crystallization or water produced during the burning of the minerals is removed by passing the sulphur dioxide through phosphorus pentoxide before freezing it down in a trap at liquid air temperature. Carbon dioxide and other highly volatile impurities are eliminated by allowing the sulphur dioxide to warm up to -85°C . (dry ice and acetone) and then evacuating the system. Mass spectrometer analyses show that no fractionation of the sulphur isotopes occurs from this procedure. Mass spectrometer analyses show the sulphur dioxide samples contain about 1 to 5% carbon dioxide.

The native sulphur and pyrite samples are easily oxidized to sulphur dioxide by the method described above. As it is not possible to prepare sulphur dioxide from sulphate minerals [gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4)] by burning alone, it is necessary to convert them to free sulphur or a combustible sulphide. Calcium sulphide is prepared by roasting equal weights of the sulphate mineral and finely powdered carbon at 800° to 1000° C. for about 24 hr. The calcium sulphide is dissolved in a slightly acidic solution to form calcium hydrosulphide ($\text{Ca}(\text{HS})_2$), which, after being filtered from the unreacted sulphate and carbon, is precipitated as lead sulphide or oxidized to free sulphur by iodine in potassium iodide solution. Repeated preparations of sulphur dioxide samples were made to check any possible variation in the isotopic abundance of the sulphur and in no case could any variation in the $\text{S}^{32}/\text{S}^{34}$ ratio be attributed to the preparation procedures.

Three different sources of sulphur were analyzed from sulphuretted water collected from various parts of southern Ontario, namely, soluble hydrogen sulphide, soluble sulphates, and free sulphur which precipitated from the water. The hydrogen sulphide is boiled out of solution, precipitated as lead sulphide, and burned to sulphur dioxide as previously described. The free sulphur is oxidized to sulphur dioxide by burning also. After the hydrogen sulphide is removed from the water, the total sulphate content is precipitated and filtered from a hot, slightly acidic solution as lead sulphide. As in the conversion of calcium sulphate, equal weights of lead sulphate and carbon are roasted at 800° to 1000° C. for 24 hr. Part of the lead sulphate is reduced directly to lead, but the majority of it is reduced to lead sulphide. The lead sulphide is separated from the remaining material by adding concentrated phosphoric acid to the mixture, converting the lead sulphide to hydrogen sulphide, which is reprecipitated as lead sulphide. Sulphur dioxide is then prepared by burning the lead sulphide.

The coal and petroleum samples were obtained from the gaseous products liberated in the destructive distillation of coal (from West Virginia) and the cracking of second distillate oil (from Venezuela) respectively. The hydrogen sulphide in these gaseous products was precipitated as lead sulphide and burned as such to sulphur dioxide.

Mass Spectrometry

The relative isotopic abundance data given in this paper were obtained with a 180 degree direction focusing mass spectrometer of the Nier type (14). Automatic recording (6) was used and the electronic units have been described previously (5, 11, 12).

Sulphur dioxide gas was used in the mass spectrometer in the analysis of the sulphur isotopes. It was more convenient to study the molecular ions SO_2^+ , but a few samples were also investigated as SO^+ ions. The latter results agreed with the values obtained for SO_2^+ ions. This agreement indicates that the samples and the mass spectrometer tube were free from impurities in the

SO_2 mass ranges. The lack of peaks in the spectrogram of residual gases in the tube and the absence of other masses in the SO_2 and SO spectrograms were further evidence of the purity of the samples. The contributions of the SO_2^+ ions to the ion currents appearing at the different mass numbers (see Fig. 1) are shown in Table I. Rare combinations such as $\text{SO}^{17}\text{O}^{17}$ and $\text{SO}^{17}\text{O}^{18}$

TABLE I
 SO_2^+ , SO^+ SPECTRUM

Mass number	Isotope combinations
SO_2^+ 64	$(\text{S}^{32}\text{O}^{16}\text{O}^{16})$
65	$(\text{S}^{32}\text{O}^{16}\text{O}^{17}), (\text{S}^{32}\text{O}^{16}\text{O}^{18})$
66	$(\text{S}^{32}\text{O}^{16}\text{O}^{18}), (\text{S}^{33}\text{O}^{16}\text{O}^{17}), (\text{S}^{34}\text{O}^{16}\text{O}^{16})$
67	$(\text{S}^{34}\text{O}^{16}\text{O}^{17}), (\text{S}^{33}\text{O}^{16}\text{O}^{18})$
68	$(\text{S}^{34}\text{O}^{16}\text{O}^{18}), (\text{S}^{32}\text{O}^{18}\text{O}^{18}), (\text{S}^{36}\text{O}^{16}\text{O}^{16})$
SO^+ 48	$(\text{S}^{32}\text{O}^{16})$
49	$(\text{S}^{33}\text{O}^{17}), (\text{S}^{33}\text{O}^{16})$
50	$(\text{S}^{32}\text{O}^{18}), (\text{S}^{33}\text{O}^{17}), (\text{S}^{34}\text{O}^{16})$
51	$(\text{S}^{33}\text{O}^{18}), (\text{S}^{34}\text{O}^{17})$
52	$(\text{S}^{34}\text{O}^{18}), (\text{S}^{36}\text{O}^{16})$

are not shown. The $\text{S}^{32}/\text{S}^{34}$ ratio as determined from the SO_2^+ spectrum may be obtained directly from the mass spectrometer ratio of mass 64/mass 66.

$$\frac{(64)}{(66)} = \frac{\text{S}^{32}\text{O}^{16}\text{O}^{16}}{\text{S}^{34}\text{O}^{16}\text{O}^{16} + (\text{S}^{32}\text{O}^{16}\text{O}^{18})} = \frac{1}{2 \cdot \frac{\text{O}^{18}}{\text{O}^{16}} + \frac{\text{S}^{34}}{\text{S}^{32}}}$$

The contribution of $(\text{S}^{33}\text{O}^{16}\text{O}^{17})$ to the mass 66 peak is negligibly small and may be neglected.

$$\frac{\text{S}^{32}}{\text{S}^{34}} = \frac{1}{\frac{(66)}{(64)} - 2 \cdot \frac{\text{O}^{18}}{\text{O}^{16}}}$$

where $(66)/(64)$ is the ratio of the ion currents at masses 66 and 64, respectively, and may be obtained directly from the spectrograms (Fig. 1).

Similarly from the SO^+ spectrum we have

$$\frac{\text{S}^{32}}{\text{S}^{34}} = \frac{1}{\frac{(50)}{(48)} - \frac{\text{O}^{18}}{\text{O}^{16}}}$$

The same oxygen was used in the preparation of all samples, so that the $\text{O}^{18}/\text{O}^{16}$ ratio could be considered as constant. The value of this ratio was taken as 0.00208 for tank oxygen as previously determined (16).

The problem of measuring relative isotopic abundances to a high order of precision is quite different from that of the determination of absolute isotopic abundances, as has been discussed previously (15). Although absolute mass spectrometer abundance ratios vary by $\pm 0.5\%$ over a period of time, a relative precision of $\pm 0.05\%$ can be obtained by comparing each sample to a standard. The procedure is to analyze the standard, the sample, and the

standard again as quickly as possible. If the two sets of results for the standard sample agree within the limits of precision for a single set, then the comparison with the middle set is considered satisfactory. The relative

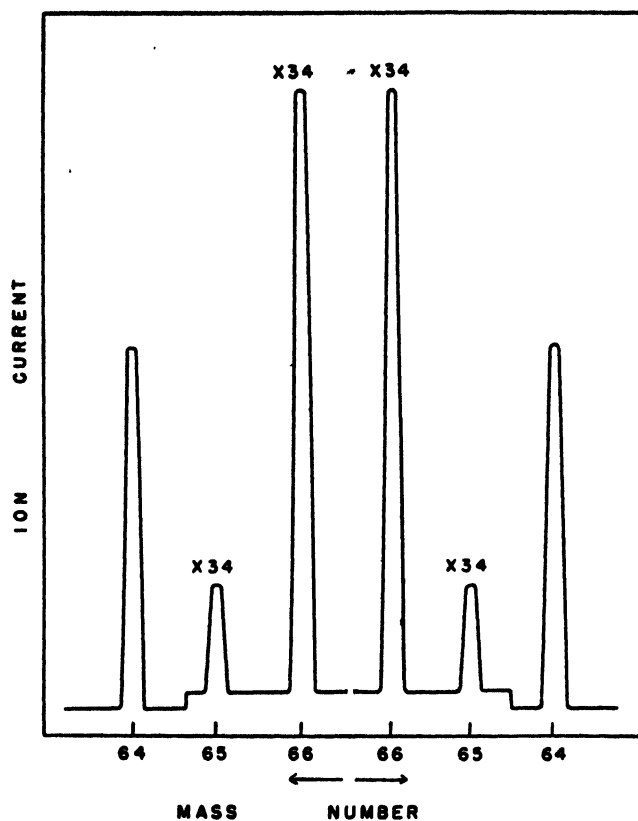


FIG. 1. Mass spectrogram of isotopes of sulphur (S^{36} excluded) with typical double record obtained by scanning in both directions.

precision obtained is, of course, dependent on the agreement of the two standard analyses. The use of automatic recording equipment with continuous scanning facilitates the rapid production of spectrograms as shown in Fig. 1. One ratio of mass 64/mass 66 is obtained from such a spectrogram, and six ratios give a mean value with a precision of $\pm 0.05\%$ or better.

Results

Although there are four isotopes of sulphur, S^{32} , S^{33} , S^{34} , and S^{36} , it was convenient to follow changes in the ratio of only two of them, namely S^{32} and S^{34} . Most of the results are therefore given in terms of this ratio. Fig. 1 shows a typical recorded mass spectrogram from a set of which the S^{32}/S^{34} ratio is determined (with a precision of 0.05%). A large number of samples have been investigated. The results obtained for pyrite minerals, free or native sulphur, sulphate minerals, and sulphuretted water (hydrogen sulphide) samples are given in Tables II, III, IV, and V, respectively. Samples of

TABLE II
SULPHUR ISOTOPE ABUNDANCE DATA FOR PYRITE MINERALS

Mineral	Location	Age	Crystallization temperature, °C.	S ³³ /S ³⁴ ratio
Pyrite	Dubuque, Iowa	Late Paleozoic	450	22.465 ± 0.010
Pyrite with fluorite and calcite	Tilley Foster Mine, Brewster, N.Y.	Pre-Cambrian	—	22.465 ± 0.005
Pyrite with pyrrhotite	Kisbanya, Roumania		230	22.355 ± 0.005
Pyrite in chlorite	Rhode Island	Primary	510	22.345 ± 0.010
Pyrite with scheelite	Mill City, Nevada		535	22.275 ± 0.005
Pyrite and magnetite	Dognaska, Hungary	Early Tertiary	510	22.275 ± 0.020
Pyrite	Echo Twp., Ont.	Pre-Cambrian	590	22.235 ± 0.010
Pyrite	Tyrol		120	22.235 ± 0.010
Pyrite in schist	Freiberg, Saxony	Late Paleozoic	80	22.200 ± 0.010
Pyrite with bornite	Magdalena, N. Mex.		540	22.200 ± 0.010
Pyrite	Madoc, Ont.			22.165 ± 0.010
Pyrite with enargite	Cerro de Pasco, Peru	Early Tertiary	360	22.120 ± 0.005
Pyrite	Park City, Utah	Jurassic	475	22.120 ± 0.010
Pyrite	Milton, Vermont		120	22.120 ± 0.010
Pyrite	Joplin, Missouri		100	22.070 ± 0.010
Pyrite	Lanark County, Ont.		—	22.010 ± 0.010
Pyrite	Gellivara, Sweden	Pre-Cambrian	635	22.010 ± 0.010
Pyrite in chlorite	Chester, Vermont	Primary	510	22.000 ± 0.010
Pyrite	Franklin, N.J.	Pre-Cambrian	105	21.610 ± 0.010

TABLE III
SULPHUR ISOTOPE ABUNDANCE DATA FOR NATIVE SULPHUR

Mineral	Location	S ³³ /S ³⁴ ratio
Native sulphur	Gulf of Mexico	22.370 ± 0.010
Native sulphur	Gulf of Mexico	22.290 ± 0.005
Native sulphur	Sicily	22.030 ± 0.010
Native sulphur	Copper Cliff Mine, Sudbury, Ont.	22.230 ± 0.010
Native sulphur	Italy	22.070 ± 0.010
Native sulphur	Locality I (unknown)	21.860 ± 0.010

TABLE IV
SULPHUR ISOTOPE ABUNDANCE DATA FOR ROCK SULPHATES

Mineral	Location	S ³³ /S ³⁴ ratio
Anhydrite (CaSO ₄)	Berchtesgaden, Bavaria	22.120 ± 0.005
Gypsum (CaSO ₄ · 2H ₂ O)	Caledonia, Ont.	22.035 ± 0.010
"	Cayuga, Ont.	21.845 ± 0.005
"	Parrsboro, N.S.	22.015 ± 0.010
"	Lockport, N.Y.	21.690 ± 0.010
"	Crystal Falls, Mich.	21.595 ± 0.010
"	Mt. Healy, Ont.	21.785 ± 0.005

TABLE V

SULPHUR ISOTOPE ABUNDANCE DATA FOR HYDROGEN SULPHIDE FROM SULPHUR WATER

Location of sulphur water (H ₂ S)	Description of water	S ³² /S ³⁴ ratio
Port Ryerse, Ont., 270 ft. well	Dirty grey, oily	22.415 ± 0.010
Port Stanley, Ont., 300 ft. well	Dirty green	22.215 ± 0.010
Dorchester, Ont., 150 ft. well	Crystal clear	22.705 ± 0.010
Dundas, Ont., 150 ft. well	Crystal clear	22.610 ± 0.005
Tillsonburg, Ont.	Slight turbidity	22.180 ± 0.005

sulphur from coal, petroleum, and other sulphides have also been investigated. These results and those given in the tables are tabulated diagrammatically in Fig. 2. It is seen that the S³²/S³⁴ ratio varies by as much as 5% from the

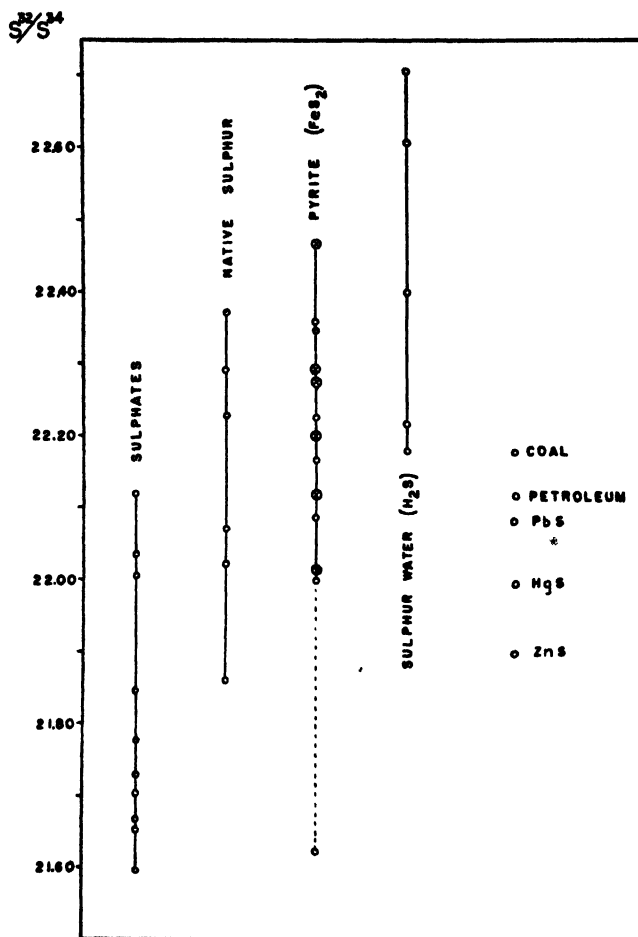


FIG. 2. Isotopic distribution of sulphur 34 in nature.

extreme low value of the sulphates to the highest ratio obtained for hydrogen sulphide in well water. In general, sulphates have a high S³⁴ content or a low S³²/S³⁴ ratio whereas hydrogen sulphide in well water is low in S³⁴ and has

a high S^{32}/S^{34} ratio. Table VI gives the results obtained for a series of sulphur containing minerals which have been sampled several times to determine isotopic uniformity of similar crystals. These results indicate variations only slightly greater than the internal precision of the mass spectrometer measurements.

TABLE VI
SULPHUR ISOTOPE ABUNDANCE DATA SHOWING ISOTOPIC UNIFORMITY OF SAMPLES

Mineral	Location	Sample No. (separate preparations)	S^{32}/S^{34} ratio*	Average
Pyrite (FeS_2)	Franklin, N.J.	1	21.620	21.610
		2	21.580	
		3	21.630	
Anhydrite ($CaSO_4$)	Berchtesgaden, Bavaria	1	22.095	22.110
		2	22.120	
		3	22.120	
Gypsum ($CaSO_4 \cdot 2H_2O$)	Lockport, N.Y.	1	21.895	21.920
		2	21.945	
Native sulphur	Sicily	1	22.310	22.300
		2	22.290	
Native sulphur	Locality I (unknown)	1	22.605	22.630
		2	22.655	
Native sulphur	Dorchester, Ont.	1	22.705	22.705
		2	22.705	
H_2S from sulphur water	Port Ryersee, Ont.	1	22.690	22.675
		2	22.655	

* Precision of each determination is 0.05%.

Variations in the Abundances of S^{32} , S^{33} , S^{34} , and S^{36}

In one experiment two different samples of sulphur were compared both in regard to the S^{32}/S^{33} and S^{32}/S^{34} ratios. The isotopic abundance data obtained are given in Table VII.

TABLE VII
SULPHUR ISOTOPE ABUNDANCE DATA FOR TWO
SAMPLES COMPARED (S^{36} EXCLUDED)

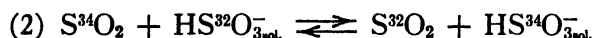
Sample	Ratio	
	S^{32}/S^{33}	S^{32}/S^{34}
1	127.25 ± 0.05	22.660 ± 0.005
2	125.20 ± 0.05	21.925 ± 0.005
Percentage difference	1.64	3.35

According to these results the percentage difference in isotopic ratio doubles as the percentage mass difference between the isotopes doubles. Although the variations in the S^{32}/S^{36} ratios have not been measured, it is expected that

these will be four times the corresponding variations in the S^{32}/S^{33} ratio or double those of the S^{32}/S^{34} ratio. This is in accordance with theoretical considerations where isotopic fractionation occurs owing to differences in the thermodynamic properties of isotopic substances. Further, the experimental exchange constant for the isotopic reaction



at 25° C. determined previously (14) is 1.039 as compared to 1.019 for the reaction



This means that in the above equilibrium process S^{34} and S^{36} are favored in the solution phase by 2 and 4% respectively. The results of Table VII are, therefore, further proof that the isotopes of sulphur are fractionated in natural processes because of differences in their chemical and physical properties. Certainly any nuclear process would be specific for one isotope. The maximum variation in the S^{32}/S^{34} ratio of about 5% (see Fig. 2) indicates a corresponding variation in the S^{32}/S^{36} concentration of 10%.

Crystallization Temperature and Isotopic Abundance

The crystallization temperatures given in Table II for the various pyrite samples investigated were determined for us by Mr. H. S. Scott of the McMaster University Geology Department. His measurements were made with a pyrite geothermometer developed by Prof. F. Gordon Smith (13) of the University of Toronto. An examination of the data in Table II would indicate little if any correlation between pyrite crystallization temperature and the isotopic content of the sulphur. However, this is not surprising since the pyrite samples came from widely different geological formations and geographical locations and have therefore had different histories.

Table VIII, on the other hand, gives isotopic abundance data for pyrite crystals removed from the same mineral specimen. In each case the crystals

TABLE VIII

VARIATIONS IN THE ISOTOPIC ABUNDANCE BETWEEN FINE AND COARSE CRYSTALS FROM THE SAME PYRITE SPECIMEN

Mineral	Location	Fine crystals		Coarse crystals	
		S^{32}/S^{34} ratio	Temp., ° C.	S^{32}/S^{34} ratio	Temp., ° C.
Pyrite with chalcopyrite and calcite	Gilman, Colo.*	22.155 ± 0.005	235	22.220 ± 0.010	185
Pyrite	Larga Mine, Zalanthna, Hungary	22.155 ± 0.005	210	22.225 ± 0.010	135

Chalcopyrite crystals from Gilman, Colo. have S^{32}/S^{34} ratio of 22.261.

graded from fine in the center to coarse on the outside (see Fig. 3). The results indicate that there is a definite variation in the isotopic abundance of the sulphur from the center out. Further, the pyrite geothermometer temperature measurements indicate a corresponding variation in crystallization temperature from the fine to the coarse crystals (in the same specimen). This phenomenon therefore can account for many small variations in the isotopic ratio of sulphur. The large variations found for pyrite samples in Table II are probably due to other isotopic fractionation processes. In this regard, one pyrite mineral specimen investigated from Sayerville, N.J., did not have the usual gradation from fine to coarse crystals but had a "concretion" or round ball of fine crystals embedded in coarse crystals with a thin layer of sulphate mineral between them (see Fig. 3-a). In this case the concentration of S^{34} varied by 3%, indicating that the two kinds of pyrite although in the same specimen had been formed under quite different conditions or from sulphur of different isotopic content.

Pyrite Minerals

Some 30 samples of pyrite collected from various parts of the world were analyzed and an attempt made to correlate the variations in the isotopic content of sulphur with some definite naturally occurring phenomenon. As can be seen from Table II, no correlation exists between the variation of the isotopic abundance and the deposition age of the pyrite. However, these negative results are not surprising in that the samples of pyrite were collected from such widespread parts of the world and crystallization conditions are entirely different.

It is interesting to note that the one pyrite sample whose S^{32}/S^{34} ratio is 2% lower than the average pyrite (see Fig. 2) came from the unique mineral deposits at Franklin, N.J., commonly referred to as Franklin Furnace. Over 100 minerals have been found there, at least a dozen of which have not been noted elsewhere. Geologists agree that the presence of spinel minerals indicates high temperature formation and that the deposits of pyrite may have taken place at two different times. However, there are various theories as to the exact origin of the mineral deposits at Franklin Furnace. C. Palache (10) describes the ore bodies as of metasomatic origin, occurring in Pre-Cambrian limestone which later underwent regional metamorphism. He suggests that the ore solutions derived their metallic constituents from the oxidation of earlier deposits of mixed sulphides. Although it is more generally thought that the mineral deposits came about by a magmatic intrusion into the limestone, Palache claims that the only clear evidence of direct introduction of magmatic materials is found to be in the contact zones about the pegmatites which were formed far later than the ore deposits themselves. The fact that the S^{32}/S^{34} ratio for the Franklin, N.J., pyrite lies at the bottom of the sulphate range may mean that the iron was in the form of a sulphate at one time and later was converted to pyrite.



3



3a

FIG. 3. *Pyrite mineral showing fine center crystals and coarse outer crystals.*

FIG. 3a. *Pyrite mineral showing concretion.*

Sulphate and Hydrogen Sulphide Waters

Although the S^{34} content of gypsum deposits, Table IV, vary by 2%, the concentration of S^{34} for sulphates is consistently high. A further comparison of isotope abundance data for SO_4^{2-} , S^0 , and H_2S present together in well water is given in Table IX. The part of southern Ontario from which the samples were collected is a natural gas area, the gas being contained largely in the Guelph limestone below the surface.

TABLE IX

A COMPARISON OF ISOTOPE ABUNDANCE DATA FOR SO_4^{2-} , S^0 , AND H_2S PRESENT TOGETHER IN WELL WATER FROM DIFFERENT LOCATIONS

Sample	Dorchester, Ont.	Tillsonburg, Ont.	Port Ryerse, Ont.	Port Stanley, Ont.
	S^{32}/S^{34} ratio			
H_2S	22.705 ± 0.010	22.180 ± 0.010	22.400 ± 0.010	22.215 ± 0.010
SO_4^{2-}	21.735 ± 0.010	21.715 ± 0.010	21.650 ± 0.010	21.585 ± 0.010
S^0	22.705 ± 0.005	22.285 ± 0.010	—	—

As in the case of the gypsum deposits, the sulphates in solution are again enriched in the heavy isotopes of sulphur. The hydrogen sulphide and free sulphur present in the same solutions contain from 2 to 5% less S^{34} than the sulphates. The free sulphur formed from these solutions by air oxidation of hydrogen sulphide has the same isotopic content as the hydrogen sulphide. This is an interesting result but not altogether unexpected. Reactions 1 and 2 above have been investigated extensively and could be a factor where sulphite solutions are in equilibrium with sulphur dioxide at some state in the history of the samples. Further, theoretical calculations by Urey (17) show that heavier isotopes of chlorine should in chemical exchange processes be favored in compounds where chlorine is in the higher valence state. Thus ClO_4^- would have the greatest tendency to concentrate Cl^{37} providing a chemical exchange mechanism can be found and equilibrium established. By analogy the heavier isotopes of sulphur and in particular S^{34} would be favored in the following valence states to an increasing extent, S^{2-} , SO_3^{2-} , SO_4^{2-} . This reasoning would seem to account for the high S^{34} content of sulphates. Partition function ratios for the isotopic substances $H_2S_{(gas)}$, S^{2-} , and SO_4^{2-} are now being calculated. From these values the exchange constants for possible isotopic reactions may be calculated.

Since hydrogen sulphide water samples listed in Tables V and IX are all from a natural gas area in southern Ontario, it is reasonable to assume that the hydrogen sulphide is organic in origin and diffuses up from the gas strata below. In this regard it is interesting to note that the two shallow wells

(water nearest the surface and furthest from the gas bearing strata) have the highest S^{32}/S^{34} ratio. If the hydrogen sulphide gas diffuses through rocks or fissures, then some fractionation can be expected since the isotopic molecules will have different diffusion rates. This could account for the low S^{34} content in the water nearest the surface of the ground. In addition, some fractionation could result from the exchange of sulphur isotopes between hydrogen sulphide gas and S^{2-} or HS^{-} ions in solution. Preliminary statistical calculations in this laboratory by H. Bowlden (2) for this exchange reaction indicate that the heavier isotopes are favored in the gaseous phase. This would mean that sulphur water washed with hydrogen sulphide would be depleted in S^{34} . The low S^{34} content of hydrogen sulphide well water could therefore be due to a combination of gaseous diffusion and chemical exchange fractionation. Further investigations of hydrogen sulphide water samples and hydrogen sulphide from natural gas in a given locality are in progress.

Discussion

From the results of this paper it is clear that relatively large variations occur in the abundances of the sulphur isotopes. In future, isotope abundance tables must state the origin of the samples investigated where values are given to better than a few per cent.

In the case of carbon and sulphur, we do not have a large reservoir of material of constant isotopic composition to provide a base level from which isotopic variations in other compounds can be reckoned, as, for example, the sea, in the case of the oxygen isotopes. For this reason, less meaning can be attached to the many variations found at the present time. However, the experimental and theoretical investigations which have been made show that these variations in isotopic abundances are significant and have important implications in physics, chemistry, biology, and geology. The changes in isotopic ratios that occur are undoubtedly related to the differences in chemical properties and will depend on chemical and physical processes that occur in nature or in the laboratory. A further means is therefore provided for tracing out the mechanism of natural processes and for determining the origin of certain natural materials containing sulphur. Isotopic data of high precision have already made a notable contribution to chemistry and geology and promise to be very fruitful in the future.

Acknowledgments

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A THEORY FOR CREEP OF CERAMIC BODIES UNDER CONSTANT LOAD¹

BY PETER GIBBS AND HENRY EYRING

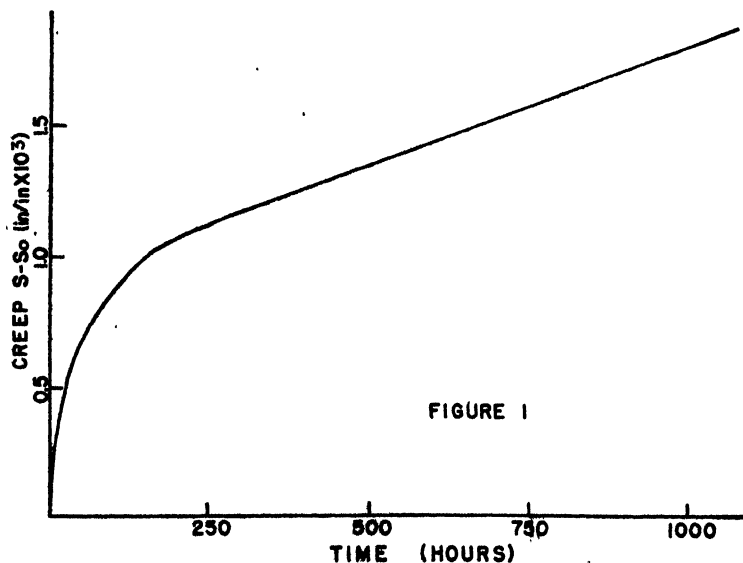
Abstract

The plastic flow and elastic behavior of ceramic materials is treated using a statistical mechanical relaxation theory. It is found necessary to treat creep as involving two, and, in some cases, three relaxation mechanisms. The methods necessary for treating such non-Newtonian flow are developed here for creep for the first time. The results obtained are in accord with expectations on the basis of reports of others for flow at constant rate of loading and constant rate of strain for other materials.

Introduction

Professor Thorvaldson has been an outstanding pioneer in various aspects of chemistry and especially in the field dealing with the nature and properties of cement. A theory of the plastic and elastic deformation of related substances forms the basis of the material presented here.

In creep tests a constant tensile stress is applied axially to a cylindrical test specimen. The elongation per unit of length between two gauge marks near the center of the specimen is called creep. A typical time-elongation curve due to Norton (9) is reproduced in Fig. 1. The data relative to each



curve in this paper are collected in Table I. There is an instantaneous elongation at the time of application of the load which is not shown in Fig. 1. A decrease in specimen cross section is observed as elongation proceeds.

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Contribution from the University of Utah, Salt Lake City, Utah, U.S.A. This paper is based on a research program conducted at the University of Utah in co-operation with the Office of Naval Research, U.S. Navy Department.

TABLE I

Fig.	Temp.	Stress	Composition	Reference	Author's designation	Parameters calculated from curve
1	1060° C.	50 lb./in. ²	$\left\{ \begin{array}{l} \text{Potash feldspar} \quad 25\% \\ \text{Flint} \quad 25\% \\ \text{No. 1 English China clay} \quad 35\% \\ \text{Kentucky ball clay} \quad 15\% \end{array} \right.$	(9)		
3A	900° C.	1000 lb./in. ²	Same as 1	(9)		$\left\{ \begin{array}{l} G = 1.59 \cdot 10^{10} \text{ dynes/cm.}^2 \\ \Delta F_1^{\ddagger} = 1.12 \cdot 10^5 \text{ cal./mole} \\ \Delta F_2^{\ddagger} = 1.15 \cdot 10^5 \text{ cal./mole} \\ V_{h1} = 1.02 \cdot 10^{-20} \text{ cm.}^3 \\ V_{h2} = 5.64 \cdot 10^{-20} \text{ cm.}^3 \end{array} \right.$
3B	900° C.	400 lb./in. ²	Same as 1	(9)		
4A	1350° C.	2000 gm./cm. ²	"Raw Clay A"	(10)	# 354	
4B	1400° C.	1000 gm./cm. ²	"Raw Clay A"	(10)	# 225	
4C	1060° C.	50 lb./in. ²	Same as 1	(9)		$\left\{ \begin{array}{l} G = 2.25 \cdot 10^9 \text{ dynes/cm.}^2 \\ K_1 \alpha_1 = 7.41 \cdot 10^{-17} \text{ cm.}^2/\text{dyne.} \\ \text{sec.} \\ K_2 \alpha_2 = 1.98 \cdot 10^{-18} \text{ cm.}^2/\text{dyne.} \\ \text{sec.} \end{array} \right.$
4D	1450° C.		German siliceous clay	(10)	Fig. 4	
4E	1350° C.	2000 lb./in. ²	$\left\{ \begin{array}{l} 60\% \text{ "Clay A"} \\ 40\% \text{ fine grog} \end{array} \right.$	(10)	# 306	
5	1060° C.	50 lb./in. ²	Same as 1	(9)		$\left\{ \begin{array}{l} G = 2.11 \cdot 10^9 \text{ dynes/cm.}^2 \\ K_1 \alpha_1 = 6.38 \cdot 10^{-17} \text{ cm.}^2/\text{dyne.} \\ \text{sec.} \\ K_2 \alpha_2 = 3.87 \cdot 10^{-18} \text{ cm.}^2/\text{dyne.} \\ \text{sec.} \end{array} \right.$
6A	1350° C.	2000 lb./cm. ²	"Raw clay A"	(10)	# 326	
6B	1800° F.	6800 lb./in. ²	$\left\{ \begin{array}{l} \text{MgO} \quad 19.6\% \\ \text{BeO} \quad 20.3\% \\ \text{ZrO}_2 \quad 60.1\% \end{array} \right.$	(3)	Fig. 7	
6C	1800° F.	7000 lb./in. ²	$\left\{ \begin{array}{l} \text{MgO} \quad 9.8\% \\ \text{BeO} \quad 10.2\% \\ \text{ZrO}_2 \quad 80.0\% \end{array} \right.$	(3)	Fig. 11(c)	
6D	1350° C.	1000 gm./cm. ²	40% "Clay A" 60% grog	(10)	# 367	
7			"Siliceous clay C"	(10)	Fig. 5	

Theory

Deformation of any substance involves the transfer of material through the deformed body. This process may be thought of as the migration of density fluctuations (1) within the material. Inasmuch as a substance may be a

very complicated system of crystalline grains, amorphous matrix material and flaws, the fluctuations in density will, of course, vary much as to type. They may be clumps of atoms, gaps between atoms, or empty sites, including the variations in atomic spacing usually spoken of as metallurgical dislocations (11). The system of active fluctuations may differ considerably from one instant to the next. Understanding this, we shall speak of these fluctuations as though they were particles. Whatever their nature, each fluctuation will have an equilibrium position at a potential energy minimum. Structural details, such as grain boundaries, etc., manifest themselves in changes in the shape of the potential energy surfaces which govern the motion of fluctuations. For our purpose, the system is completely specified if the potential energy surfaces of all the fluctuations contributing to the deformation at each instant are known.

Fluctuations tend toward equilibrium, but they may never attain it during the lifetime of most ceramic bodies. High temperatures, such as those associated with firing, tend to introduce an equilibrium number of density fluctuations corresponding to the particular temperature. A temporary state of internal or external stress may alter the number of these fluctuations present. In general, the history of a specimen may introduce non-equilibrium fluctuations which persist for long periods because of high potential energy barriers (4) surrounding them.

An applied force modifies the potential energy surfaces, shifting relative equilibrium positions slightly. Since there are no potential barriers against assuming these new equilibrium positions, the cumulative effect is an instantaneous deformation of the specimen upon application of the force. There is a return force on each fluctuation equal to the potential gradient of the unmodified barrier at the new equilibrium position. This condition is similar to Hooke's law and may be represented by a mechanical spring obeying the relation

$$f = GS, \quad (1)$$

where $f \equiv$ force per unit area,

$G \equiv$ a constant,

$S \equiv$ elongation per unit length.

With the passage of time, there is a net migration of fluctuations over their barriers in a direction to relieve stress. The rate of passage of such a system over a potential barrier is (5, 12)

$$\frac{dN^\ddagger}{dt} = \frac{2\kappa kT}{h} \exp\left(-\frac{\Delta F^\ddagger}{RT}\right) \sinh\left(\frac{V_h f}{2kT}\right), \quad (2)$$

$N^\ddagger \equiv$ Number of flow units passing over the barrier;

$\kappa \equiv$ Transmission coefficient for passage over the barrier;

$k \equiv$ Boltzmann constant;

$R \equiv$ Gas constant

ΔF^\ddagger \equiv Free energy difference in the absence of the applied stress between the equilibrium position and the "activated state" at the top of the barrier;

f \equiv Applied force per unit area;

V_h \equiv The coefficient by which the force must be multiplied to give the work done by the stress in a single passage over a potential barrier. It has the dimensions of volume and has often been called the "volume of the hole" for flow.

The elongation rate of a chain of units along the S axis, each of which slips in this manner, is

$$\frac{dS}{dt} = \frac{d}{dt} \left(\frac{N^\ddagger \lambda}{\lambda'} \right) = \frac{2\kappa K T \lambda}{h \lambda'} \exp \left(-\frac{\Delta F^\ddagger}{RT} \right) \sinh \left(\frac{V_h f}{2kT} \right) \equiv K \sinh \alpha f, \quad (3)$$

where

S \equiv elongation per unit length;

λ \equiv S component of the distance between successive equilibrium positions of a flow unit;

λ' \equiv distance along the direction of slip between successive locations where slip occurs;

$$K \equiv \frac{2\kappa K T \lambda}{h \lambda'} \exp \left(-\frac{\Delta F^\ddagger}{RT} \right);$$

$$\alpha \equiv \frac{V_h}{2kT}.$$

A mechanism which exhibits this slip property is called a viscous element or "dashpot."

The mechanical properties of ceramic bodies are here schematically represented through network combinations of springs and dashpots, as shown in Fig. 2(a). This scheme has been used in a similar way for fibers (6), metals (2),

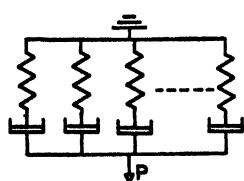


FIGURE 2(a)

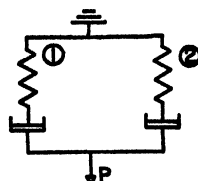


FIGURE 2(b)

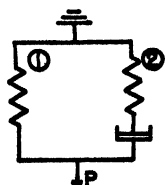


FIGURE 2(c)

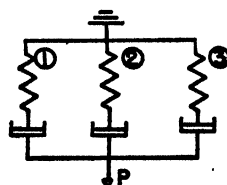


FIGURE 2(d)

FIG. 2.

glass (7) and rocks (8), etc. In general, a very large number of network branches will be required to describe the phenomena exactly. In many cases, however, two branches as shown in Fig. 2(b) will be sufficiently accurate. Equation parameters are evaluated by fitting theory to experiment. Network flow units may be referred to as "generalized fluctuations", since, when the network does represent the actual system, each flow unit is an appropriate average for a variety of individual fluctuations. Flow patterns, and hence characteristic parameters of flow units depend upon the shape and cross-sectional area of the macroscopic specimen.

Calculations for the Two-Branch Model

In general, a satisfactory method of solution of the two-branch model may be obtained by considering the following: When the load is applied the two parallel springs instantly elongate, while the dashpots slip at finite velocity. Hence the initial division of stress between the two branches is determined only by the relative spring constants. The fact that the creep curve (Fig. 1) is not a straight line as it proceeds to the left indicates that one dashpot is flowing faster than the other. As it flows, stress is being transferred from the faster to the more slowly moving dashpot until their rates are the same, and the curve finally becomes a straight line. The stress is then divided between the two branches according to the relative dashpot parameters, and is independent of the spring constants. For creep, then, stress in one branch is a monotonic function of the time. It will be observed below in a more exact solution of the "completely linear dashpot" case that stress in one branch is an exponential function of the time. In general, also, strain rate, the rate of dashpot flow, is an exponential function of the stress. This suggests that the slow dashpot might therefore be neglected in the early portion of the curve. In this region the model of Fig. 2(c) may be used. The subscript "1" will be used for quantities in the left branch and "2" for the right branch. It will be assumed here that the elastic constants $G_1 = G_2 \equiv G$. With more data this assumption could be improved upon. If the initial instantaneous deformation had been recorded by all observers, a more exact ratio of G_1 to G_2 could have been determined. The total applied tensile stress will be represented by P .

Case (a) when $\alpha_2 f_2 \gg 1$

In this case, for the first part of the experiment, the following equations are obtained:

$$\frac{dS}{dt} = \frac{1}{G} \frac{df_2}{dt} + K_2 \sinh \alpha_2 f_2 \approx \frac{1}{G} \frac{df_2}{dt} + \frac{K_2}{2} \exp(\alpha_2 f_2) \quad (4)$$

$$f_2 = P - f_1 = P - GS. \quad (5)$$

Thus the plotting $\log_{10} \left(\frac{dS}{dt} \right)$ against S yields the straight line

$$\log_{10} \left(\frac{dS}{dt} \right) = \left(\log_{10} \frac{K_2}{4} + \frac{\alpha_2 P}{2.3} \right) - \left(\frac{\alpha_2 G}{2.3} \right) S. \quad (6)$$

Since at $t = 0$, $f_2 = GS$, Equation (5) gives

$$(S)_{t=0} = \frac{P}{2G}. \quad (7)$$

Thus at $t = 0$ one can substitute (7) in (6) to obtain

$$\log_{10} \left\{ \left(\frac{dS}{dt} \right)_{t=0} \right\} = \log_{10} \frac{K_2}{4} + \frac{\alpha_2 P}{2.3} - \frac{\alpha_2 P}{4.6}. \quad (8)$$

At the same temperature but at different loads one obtains two expressions for (8) which by elimination yield the approximate relationship:

$$\alpha_2 = \frac{4.6 \Delta \left\{ \log \left(\frac{dS}{dt} \right)_{t=0} \right\}}{\Delta P}. \quad (9)$$

Thus from Equation (6) it may be seen that G may be evaluated from

$$\frac{\alpha_2 G}{2.3} \equiv C, \quad (10)$$

where C is the measured slope of the plot.

Next consider a method for determining α_1 . Substituting the first equality of (5) in (4) and remembering, for t large, that $\frac{df_2}{dt} = 0$ one obtains:

$$f_{1,a} = P - \frac{1}{\alpha_2} \sinh^{-1} \left\{ \frac{\left(\frac{dS}{dt} \right)_{t=\infty,a}}{K_2} \right\}, \quad (11)$$

where the subscript a denotes the quantity for creep at the lower of the above two loads; b will be used for the higher load.

For the left branch of Fig. 2(b) one also has

$$\frac{dS}{dt} = \frac{1}{G} \frac{df_1}{dt} + K_1 \sinh \alpha_1 f_1, \quad (12)$$

and as before, for the t large, $\frac{df_1}{dt} = 0$. Thus, taking the ratio of $\left(\frac{dS}{dt} \right)_{t=\infty}$ for a load a and a larger load b gives

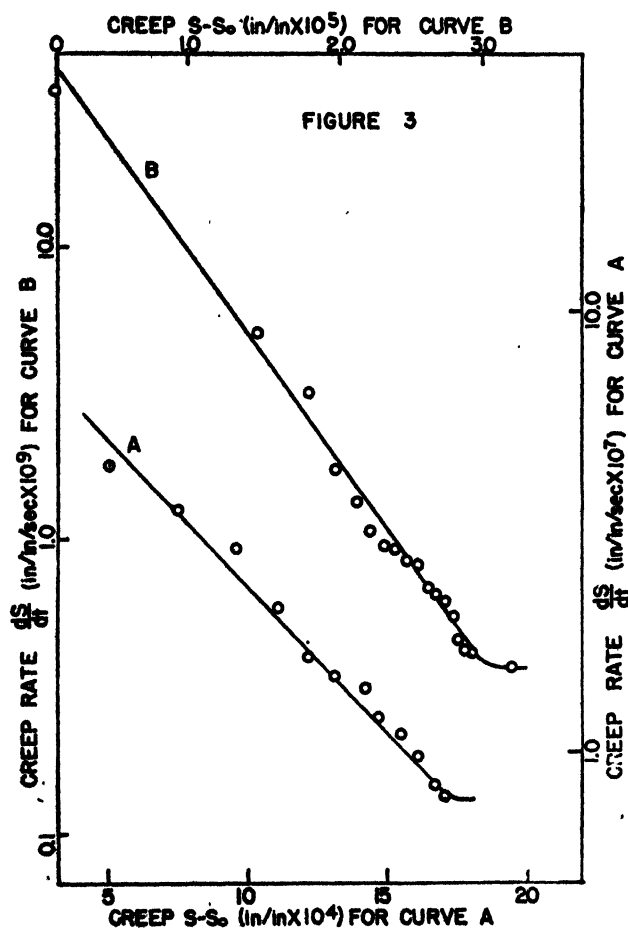
$$\frac{\left(\frac{dS}{dt} \right)_{t=\infty,a}}{\left(\frac{dS}{dt} \right)_{t=\infty,b}} = \frac{\sinh (\alpha_1 f_{1,a})}{\sinh (\alpha_1 f_{1,b})}, \quad (13)$$

from which α_1 may be determined. From (12) also one can write:

$$K_1 = \frac{\left(\frac{dS}{dt} \right)_{t=\infty,b}}{\sinh (\alpha_1 f_{1,b})}. \quad (14)$$

Values of parameters obtained by this process are a kind of average value for the two loads. In Fig. 3, $\log_{10} \left(\frac{dS}{dt} \right)$ is plotted against S for two specimens.

Values of the parameters calculated from these curves are listed in Table I. Throughout the calculations of Table I, $\frac{\kappa\lambda}{\lambda}$ has been taken as unity. Equation (6) is valid for the early part of the experiment where S is not too large, i.e., where the left branch can be treated as a pure spring. The excellence of the straight line in Fig. 3 is thus confirmation of our theory. The deviation for large S is of course a consequence of the theory, occurring when the second dashpot starts to flow.



Case (b) when $\alpha_2 f_2 \ll 1$

In this case one has:

$$\frac{dS}{dt} = \frac{1}{G} \frac{df_2}{dt} + K_2 \alpha_2 f_2 \quad (15)$$

$$f_2 = P - GS. \quad (16)$$

Combining (15) and (16) one obtains:

$$\frac{dS}{dt} = \frac{K_2 \alpha_2 P}{2} - \frac{K_2 \alpha_2 G}{2} S = D - ES \quad (17)$$

where D and E are to be read from a plot of $\frac{dS}{dt}$ against S , and where they satisfy the relations:

$$K_2\alpha_2 = \frac{2D}{P} \quad (18)$$

$$G = \frac{EP}{D}. \quad (19)$$

Next consider the further specialization of case (b) when $\alpha_1 f_1 \ll 1$. This is treated again as case (c) below by another method. For large t in Equation (15) $\frac{df_2}{dt} = 0$, whence

$$\left(\frac{dS}{dt}\right)_{t=\infty} \approx K_2\alpha_2 f_2. \quad (20)$$

Similarly, for branch 1 the following relation (21) holds when $\alpha_1 f_1 \ll 1$:

$$\left(\frac{dS}{dt}\right)_{t=\infty} \approx K_1\alpha_1 f_1 = K_1\alpha_1(P - f_2). \quad (21)$$

Eliminating f_2 between (20) and (21) gives

$$K_1\alpha_1 = \frac{\left(\frac{dS}{dt}\right)_{t=\infty} K_2\alpha_2}{K_2\alpha_2 P - \left(\frac{dS}{dt}\right)_{t=\infty}}. \quad (22)$$

In Fig. 4, $\left(\frac{dS}{dt}\right)$ is plotted against S for several specimens as is suggested by Equation (17). Only for Curve C of this figure were sufficient data available to make calculations. For this reason the scales for the other curves of Fig. 4 are arbitrary. As was the case in Fig. 3, there is excellent linearity, in accord with the theory.

Case (c) when $\alpha_1 f_1 \ll 1$ and also $\alpha_2 f_2 \ll 1$

In this case

$$\frac{dS}{dt} \approx \frac{1}{G} \frac{df_1}{dt} + K_1\alpha_1 f_1 = \frac{1}{G} \frac{df_2}{dt} + K_2\alpha_2 f_2 \quad (23)$$

$$f_2 = P - f_1. \quad (24)$$

Thus we can write:

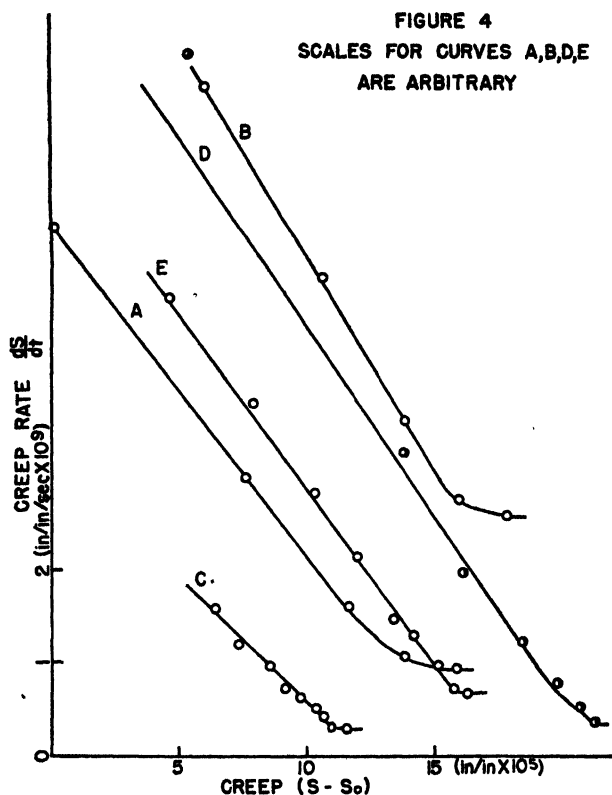
$$\frac{1}{G} \frac{df_1}{dt} + K_1\alpha_1 f_1 = -\frac{1}{G} \frac{df_1}{dt} + K_2\alpha_2 P - K_2\alpha_2 f_1. \quad (25)$$

Taking the constant of integration

$$(f_1)_{t=0} = \frac{P}{2} \quad (26)$$

in accord with our assumption that $G_1 = G_2$. The solution to (25) is thus

$$f_1 = \frac{P}{2} \frac{K_1\alpha_1 - K_2\alpha_2}{K_1\alpha_1 + K_2\alpha_2} \exp \left\{ -\frac{G}{2} (K_1\alpha_1 + K_2\alpha_2)t \right\} + \frac{K_2\alpha_2 P}{K_1\alpha_1 + K_2\alpha_2}. \quad (27)$$



Substituting (27) in (23) one obtains:

$$\frac{dS}{dt} = \frac{P}{4} \frac{(K_1\alpha_1 - K_2\alpha_2)^2}{K_1\alpha_1 + K_2\alpha_2} \exp \left\{ -\frac{G}{2} (K_1\alpha_1 + K_2\alpha_2)t \right\} + \frac{K_1\alpha_1 K_2\alpha_2}{K_1\alpha_1 + K_2\alpha_2} P. \quad (28)$$

From (28) we see that

$$\left(\frac{dS}{dt} \right)_{t=\infty} = \frac{K_1\alpha_1 K_2\alpha_2}{K_1\alpha_1 + K_2\alpha_2} P, \quad (29)$$

and its value is the limiting slope of the S versus t curve at $t = \infty$. In logarithmic form (28) may be written:

$$\log_{10} \left\{ \frac{dS}{dt} - \left(\frac{dS}{dt} \right)_{t=\infty} \right\} = A - Bt, \quad (30)$$

where

$$A \equiv \frac{P}{4} \frac{(K_1\alpha_1 - K_2\alpha_2)^2}{K_1\alpha_1 + K_2\alpha_2}, \quad (31)$$

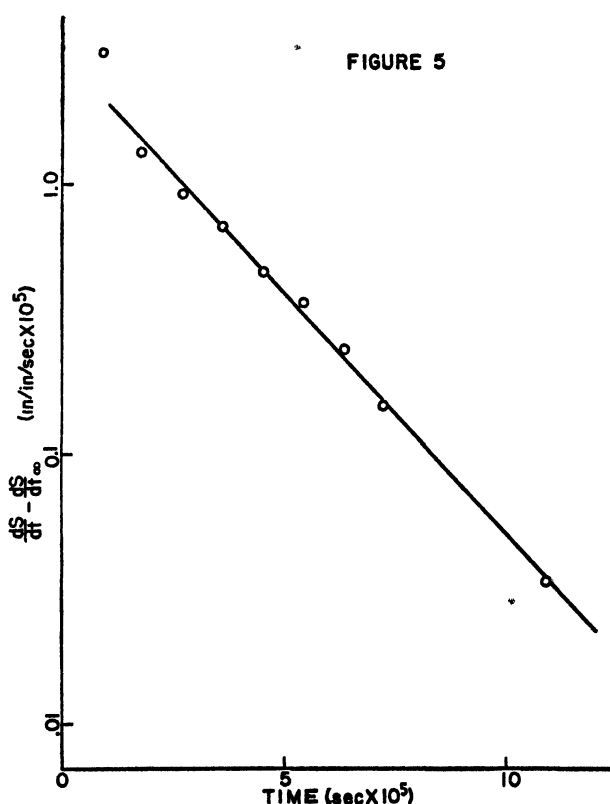
$$B \equiv \frac{G}{4.6} (K_1\alpha_1 + K_2\alpha_2). \quad (32)$$

A plot of Equation (30) for a specimen of Norton (9) is shown in Fig. 5 from which A and B may be determined for this curve. From (29), (31), and (32) the following three relations are obtained:

$$K_1\alpha_1 = \frac{2}{P} \left\{ \left(\frac{dS}{dt} \right)_{t=\infty} + A - \sqrt{A \left[A + \left(\frac{dS}{dt} \right)_{t=\infty} \right]} \right\} \quad (33)$$

$$K_2\alpha_2 = \frac{2}{P} \left\{ \left(\frac{dS}{dt} \right)_{t=\infty} + A + \sqrt{A \left[A + \left(\frac{dS}{dt} \right)_{t=\infty} \right]} \right\} \quad (34)$$

$$G = \frac{4.6B}{K_1\alpha_1 + K_2\alpha_2} \quad (35)$$



The last thing done under case (b) was to solve for the parameters in the flow system using the same data of Norton (Fig. 4C) as is used in Fig. 5 by the method just outlined. The results from Fig. 4C and Fig. 5 respectively, are recorded in Table I. As may be seen, the two quite different methods lead to substantially the same results for the characteristic parameters of the flow system.

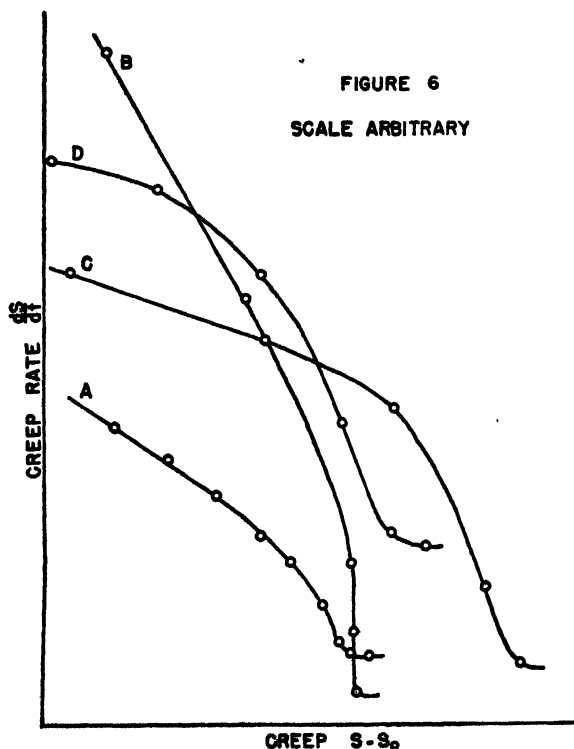
Integrating (28) one obtains:

$$S - (S)_{t=0} = \left(\frac{dS}{dt} \right)_{t=\infty} t - \frac{A}{B} (e^{-Bt} - 1). \quad (36)$$

Here the constants have been defined. From (36) it is seen that the ratio $\frac{A}{B}$ may be read from the time-elongation curve as the intercept of the $t = \infty$ asymptote with the ordinate. Fig. 1 is an experimental curve from Norton which was fitted exactly by the appropriate choice of the constants in (36).

The Three-Branch Model

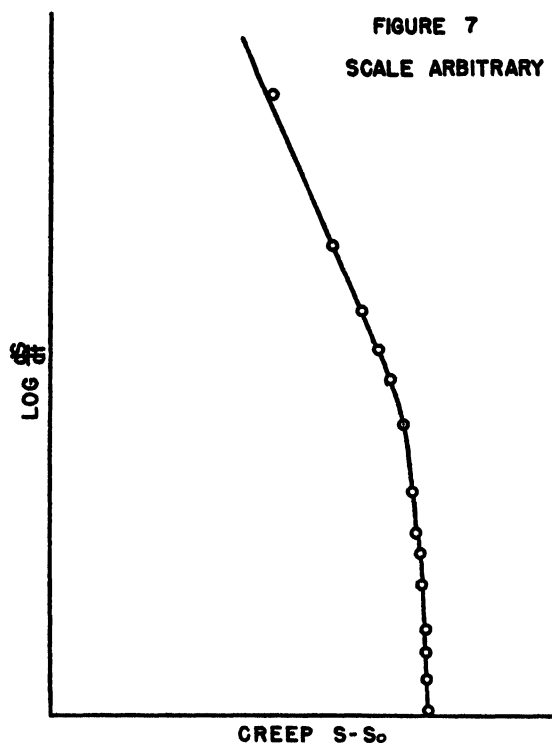
There is a group of materials for which the two-branch model is inadequate. These are illustrated in Fig. 6 where $\left(\frac{dS}{dt}\right)$ is plotted against S . Each of these curves tends to show two straight line segments before becoming horizontal



on the extreme right. Clearly, at least a three-branch model is required to explain these results. For the three-branch model of Fig. 2(d), at the beginning the two parallel springs of branches 2 and 3 act as a single spring. The curve in this region, then, should be similar to that for the two-branch case. In the second region, sufficient stress has been transferred from branch 1 to branch 2 that both dashpots are slipping. If sufficient time lapses before dashpot 3 commences to flow, the creep curve should again resemble that in the two-branch case at a correspondingly later time, since the two parallel dashpots of branches 1 and 2, when they are slipping together, act as a single dashpot. Finally, all three dashpots slipping together give a straight line for their creep curve. Actually both two-branch and three-branch creep

curves have the appearance of Fig. 1, and only an analysis such as is shown in Figs. 6 or 7 reveal their true complexity.

In our Fig. 7 have been plotted the results of an analysis of Partridge and Adams' Fig. 5 (10). These data require a three-branch model with $\alpha_1 f_1 \gg 1$ and also $\alpha_2 f_2 \gg 1$. Since dashpot 3 had not begun to flow at the end of the test, the value of $\alpha_3 f_3$ is uncertain.



The recovery effects predicted by both the two and the three-branch models were observed by the experimenters, but without giving sufficient detail that we could use it for our analysis.

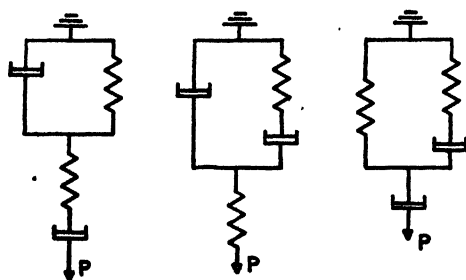


FIGURE 8

Conclusions

This analysis has for the first time applied the non-Newtonian two- and three-branch spring-dashpot models to creep. Because it was not found

possible to integrate the equations in the general case, methods were developed for calculating the flow parameters and determining the necessary model, using the differential form of the equations. The analysis proceeds almost as expeditiously as in the case where it was possible to carry out the integration. It is a matter of considerable interest that the models of Fig. 8 led us to values of the parameters which were not physically reasonable, whereas the models of Fig. 2 gave entirely reasonable parameters. This successful model was also required to explain the stress-strain results for the quite different experiments involving constant rate of loading and constant rate of strain, etc. (2, 6, 7, 8).

Acknowledgment

We wish to express our appreciation to Mr. Jay W. Frederickson for valuable discussions during the preparation of the paper.

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FRACTIONATION OF GR-S BY THE "COACERVATE" METHOD¹

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Abstract

Two different samples of synthetic rubber (GR-S) were fractionated by the "coacervate" method of Duclaux and his coworkers. This method is somewhat analogous to fractional extraction, with this difference that the polymer is in the form of a viscous liquid instead of a solid phase. One sample was refractionated into 35 subfractions. The molecular weight distribution curves show a sharp peak in the region of 40,000. The results are comparable with those of fractional precipitation.

Introduction

An accurate evaluation of the physical or chemical properties of a high polymeric material includes a determination of its molecular weight distribution. Various procedures have been employed to determine this distribution and also to prepare material of homogeneous molecular weight. A very comprehensive review of the methods of fractionation as applied to high polymers has recently been published by Cragg and Hammerschlag (5). The most practical methods which have been used in the past have invariably relied on the difference in solubility of low and of high molecular weight material. Selective precipitation of high molecular weight molecules by the addition of a nonsolvent to the polymer solution has been employed in the majority of cases. Relatively few investigators have used fractional solution in which the polymer in the solid state is extracted by a series of solvent mixtures. Bloomfield and Farmer (2) fractionated natural rubber by this method using petroleum ether and acetone, while Kemp and Peters (12) used acetone-hexane mixtures. In the synthetic high polymer field, Sebrell (17) in 1943 studied Buna S by extraction with petroleum ether - benzene solutions, and Kemp and Straitiff (13), with acetone-chloroform.

Recently a series of papers were published by Dobry, Gavoret, and Duclaux (6-11) in which they describe a method of fractionation somewhat similar to that of fractional solution, with this difference that the extractions are made from a liquid phase containing the polymer instead of from the solid material. The polymer is first dissolved in a solvent, after which a nonsolvent is added until there is separation of the solution in two phases. One phase, the supernatant liquid, contains little dissolved polymer whereas the other, of smaller volume, contains the bulk of the polymer in the form of a viscous liquid known as "coacervate," hence the name of the method. The upper layer is then decanted and an equal volume of liquid mixture, somewhat richer in solvent, is added to the remaining lower layer. This new solvent extracts additional polymer from the coacervate, the molecular weight of the polymer

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removed being dependent on the composition of the extracting medium. By repeating this procedure with mixtures of increasing solvent power, fractions of increasing molecular weights are successively extracted from the lower layer. The "coacervate" method has been used to fractionate polyvinyl acetal (9) and polyvinyl acetate (11).

The purpose of the present study was to determine the applicability of this particular method to synthetic rubber of the GR-S type and to compare the resulting fractionation with that obtained by the usual methods.

Experimental

Polymer and Solvents

The synthetic rubber used was production-line stock of regular specification (72% conversion, 50 Mooney). Prior to fractionation it was extracted by refluxing, for two periods of one hour each, with ETA (ethanol-toluene azeotrope); 100 ml. of this mixture, to which 10% water has been added, was used for every 6 gm. of polymer. The water is needed to prevent extraction of low molecular weight material (3). The polymer was then refluxed for about 30 min. with acetone and finally dried in a vacuum (3 to 5 mm. of mercury) at 23° C. for about 16 hr. The intrinsic flow times of the two samples before and after extraction were as follows:

	Before extraction	After extraction
S-2358	2.05	2.12
S-2834	2.02	2.18

Benzene—Merck Reagent brand (thiophene free) was redistilled in a bubble-cap column; boiling point range 80.0° to 80.5° C.; negative isatin test for thiophene. $N_D^{25} = 1.49720$.

Methanol—Merck Reagent brand was redistilled in a bubble-cap column; boiling point range 64.0° to 64.5° C.

PBNA—(Phenyl- β -naphthylamine) antioxidant supplied by Polymer Corporation, Sarnia, and recrystallized from alcohol: melting point, 108° C.

Experimental Methods

Viscosities were determined at $25^\circ \pm 0.02$ with two Cannon-Fenske viscometers (A. S. T. M. Series 50) chosen for their nearly identical flow times of benzene, 166.1 and 168.9 sec., respectively. In all cases the measurements were made at three or four concentrations of the solutions. The results, reported as intrinsic flow times, were obtained by extrapolation to zero concentration of $\frac{\ln t_r}{C}$ vs C , where t_r is the flow time of the solution relative to that of the pure solvent and C is the concentration in grams per 100 ml. of solution. No correction was applied for kinetic energy, as the ensuing error was found to be less than 1.5% for pure benzene and still less, obviously, for

the more viscous solutions (1, p. 31). Concentrations of polymer were found by evaporating 10-ml. samples of the solutions in light aluminum dishes and weighing; the composition of solvent mixtures could be determined to better than 0.1% from refractive index measurements. Preliminary tests had shown that the error caused by dissolved polymer, up to 0.5% in concentration, was less than the stated accuracy of these measurements.

Fractionation Procedure

The solutions were prepared by dissolving the weighed polymer in a little less than the exact quantity of benzene, filtering twice through a coarse fritted-glass funnel and making up to the final volume with the pure solvent. About 0.5 gm. of antioxidant (PBNA) was needed to prevent gel formation. Enough methanol was then added to produce a faint turbidity and the solution was immediately heated, with continuous stirring, to redissolve the precipitate. The coacervate was allowed to settle by leaving the flask in a thermostat at 25° C. for 24 hr., after which the supernatant liquid, containing the first fraction, was decanted. This operation offered no great difficulty, since the coacervate was rather firm at this stage. As the fractionation progressed, however, the coacervate grew more and more fluid and the separation became increasingly laborious. To the coacervate was now added a methanol-benzene mixture of predetermined composition, plus some antioxidant, and the whole was again made homogeneous by heating. Upon cooling and settling at 25° C. the second fraction was obtained, and so on.

Isolation of the dissolved polymer fractions for identification purposes turned out to be a delicate problem. Indeed it was found impossible to concentrate such large volumes (2.5 liters) of solvent by evaporation, even under reduced pressure, without seriously altering the polymer. The gel content rose sharply and in some cases the polymer could not be redissolved for viscosity measurements. It was therefore decided to resort to precipitation by addition of an equal volume of pure methanol containing some 10% of a 1% solution of sodium chloride in water. After about 24 hr. the milky mixture cleared and the polymer was deposited, first as a highly viscous liquid and later (with increasing molecular weight) as an amorphous solid mass. Although far from quantitative, especially for the first few fractions, this precipitation yielded a readily soluble polymer free from antioxidant and other possible impurities.

Results

Tables I and III show the results for the primary fractionation of both samples. Molecular weights were calculated by means of the equation of Carter, Scott, and Magat (4):

$$\log M = 4.89_6 + 1.49 \log [\eta] .$$

The cumulative % "S" represents the sum of the weights of all preceding fractions plus one-half that of the corresponding fraction. For reference the compositions of the various solutions are given in Tables II and IV; in the

TABLE I
PRIMARY FRACTIONATION DATA FOR S-2358

Fraction	Weight, gm.	Weight-fraction, X	Cumulative %, "S"	Intrinsic flow time, $[t]$	Product, $X \cdot [t]$	$M \times 10^{-4}$
1	4.92	0.098	4.9	0.39	0.038	1.93
2	4.07	0.082	13.9	0.58	0.048	3.46
3	7.04	0.141	25.0	0.87	0.123	6.38
4	7.06	0.141	39.1	1.23	0.173	10.9
5	6.44	0.129	52.6	1.69	0.218	17.2
6	5.48	0.110	64.5	2.31	0.255	27.4
7	2.93	0.059	72.9	2.64	0.156	33.4
8	2.62	0.052	77.9	4.24	0.220	67.7
9	1.38	0.028	82.4	4.83	0.135	82.2
10	5.18	0.103	89.0	5.96	0.620	113.0
Total	47.12	0.943			1.98 ₆	

Weight of original sample: 50 gm.
Intrinsic flow time $[t]$: 2.12.

TABLE II
COMPOSITION OF SOLUTIONS FOR S-2358

Fraction	Added mixture		Supernatant liquid	
	Volume, ml.	C ₆ H ₆ , volume %	Volume, ml.	C ₆ H ₆ , volume %
1	—	—	2870	75.2
2	2870	76.6	2825	76.5
3	2825	78.5	2625	78.5
4	2825	79.3	2815	79.4
5	2815	79.8	2525	80.0
6	2525	80.3	2650	80.5
7	2000	80.6	2000	80.6
8	2000	80.9	2000	81.1
9	2000	81.8	2000	81.5
10	—	—	200	85.1

TABLE III
PRIMARY FRACTIONATION DATA FOR S-2834

Fraction	Weight, gm.	Weight-fraction, X	Cumulative %, "S"	Intrinsic flow time $[t]$	Product, $X \cdot [t]$	$M \times 10^{-4}$
1	4.00	0.114	6.1	0.40	0.045	2.0
2	2.78	0.079	16.2	0.66	0.052	4.2
3	2.53	0.072	24.2	0.74	0.053	5.0
4	2.67	0.076	32.0	1.06	0.081	8.6
5	4.50	0.128	42.8	1.38	0.177	12.7
6	3.43	0.098	54.7	1.50	0.147	14.5
7	4.00	0.114	65.9	2.25	0.257	26.5
8	9.38	0.265	86.0	5.01	1.328	87.0
Total	33.29	0.94 ₆			2.14 ₀	

Weight of original sample: 35.00 gm.
Intrinsic flow time $[t]$: 2.18.

TABLE IV
COMPOSITION OF SOLUTIONS FOR S-2834

Fraction	Added mixture		Supernatant liquid		T, °C.
	Volume, ml.	C ₆ H ₆ , volume %	Volume, ml.	C ₆ H ₆ , volume %	
1	—	—	2060	75.7	58
2	2060	76.8	2060	76.4	54
3	1700	77.7	1700	78.0	48
4	1600	78.9	1600	78.8	42
5	1500	79.6	1500	79.9	38
6	1300	79.8	1360	80.1	36
7	1000	80.6	1000	80.9	32
8	1000	81.8	1300	82.5	25

case of S-2834 the temperatures needed to solubilize the coacervate are also given. From these data, integral distribution curves were drawn, and, by graphical method, the differential distribution curves of Fig. 1 were obtained in turn.

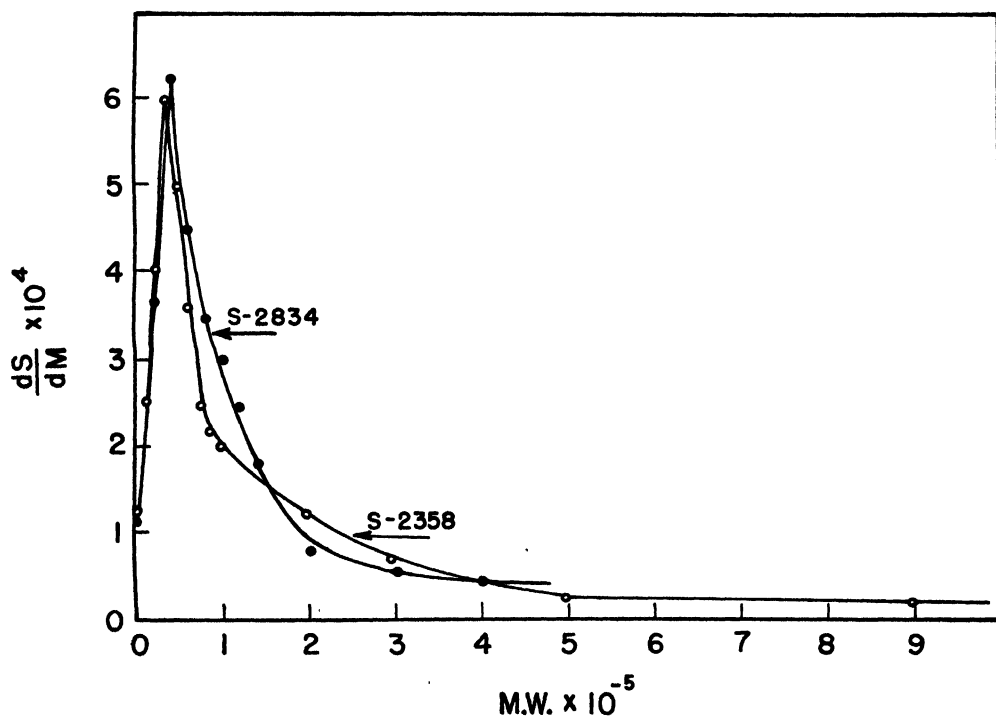


FIG. 1. Differential distribution curves for GR-S samples S-2358 and S-2834.

In order to test the efficiency of the new method each one of the primary fractions from S-2834 was refractionated into four or five subfractions, except fraction 8, which had gelled to such an extent that it was not possible to make viscosity measurements. The extent of overlapping in the primary fractions is indicated by the results of Table V and the distribution curves of Fig. 2.

TABLE V
REFRACTIONATION DATA FOR S-2834

Subfraction	Weight, gm.	Weight- fraction, X	Cumulative %, "S"	$[\eta]$	$X \cdot [\eta]$	$M \times 10^{-4}$
<i>Fraction 1</i>						
1 A	0.66	0.25	13.1	0.24	0.06 ₀	0.938
1 B	0.52	0.20	36.2	0.32	0.06 ₄	1.41
1 C	0.95	0.37	65.8	0.47	0.17 ₄	2.59
1 D	0.39	0.15	92.5	0.58	0.08 ₇	3.49
Total	2.52	0.97			0.38 ₆	
Original	2.60	1.00			0.40	
<i>Fraction 2</i>						
2 A	0.32	0.17	9.1	0.30	0.05 ₁	1.31
2 B	0.41	0.21	29.8	0.53	0.11 ₁	3.05
2 C	0.84	0.44	65.8	0.65	0.28 ₆	4.13
2 D	0.19	0.10	94.5	0.82	0.08 ₂	5.84
Total	1.76	0.92			0.53 ₀	
Original	1.92	1.00			0.66	
<i>Fraction 3</i>						
3 A	0.19	0.11	6.2	0.42	0.04 ₆	2.16
3 B	0.17	0.10	17.3	0.55	0.05 ₆	3.22
3 C	0.52	0.31	39.5	0.64	0.20	4.04
3 D	0.53	0.32	72.3	0.81	0.26	5.74
3 E	0.21	0.14	94.4	1.01	0.14	7.96
Total	1.62	0.98			0.70	
Original	1.66	1.00			0.74	
<i>Fraction 4</i>						
4 A	0.20	0.09	5.2	0.41	0.03 ₇	2.08
4 B	0.40	0.19	20.6	0.56	0.11	3.31
4 C	0.54	0.25	44.8	0.74	0.19	5.01
4 D	0.80	0.38	79.4	1.02	0.39	8.09
Total	1.94	0.91			0.73	
Original	2.13	1.00			1.06	
<i>Fraction 5</i>						
5 A	0.19	0.06	2.9	0.60	0.03 ₆	3.50
5 B	0.72	0.20	16.8	0.91	0.19	6.82
5 C	1.60	0.45	52.3	1.01	0.46	7.96
5 D	0.76	0.21	88.5	1.62	0.34	16.1
Total	3.27	0.92			1.03	
Original	3.55	1.00			1.38	
<i>Fraction 6</i>						
6 A	0.19	0.07	4.1	0.46	0.03	2.47
6 B	0.37	0.13	15.4	0.63	0.08	3.95
6 C	0.96	0.36	42.3	1.25	0.45	10.9
6 D	0.94	0.34	80.9	1.30	0.45	11.6
Total	2.46	0.90			1.01	
Original	2.74	1.00			1.50	

TABLE V—*Concluded*REFRACTIONATION DATA FOR S-2834—*Concluded*

Subfraction	Weight, gm.	Weight- fraction, X	Cumulative %, "S"	$[\eta]$	$X \cdot [\eta]$	$M \times 10^{-4}$
<i>Fraction 7</i>						
7 A	0.13	0.04	2.8	0.50	0.02	2.79
7 B	0.28	0.10	10.8	1.05	0.11	8.45
7 C	0.28	0.10	22.1	1.35	0.14	12.3
7 D	0.75	0.26	43.0	1.62	0.42	16.1
7 E	1.05	0.36	79.1	2.00	0.72	22.1
Total	2.49	0.86			1.41	
Original	2.90	1.00			2.25	

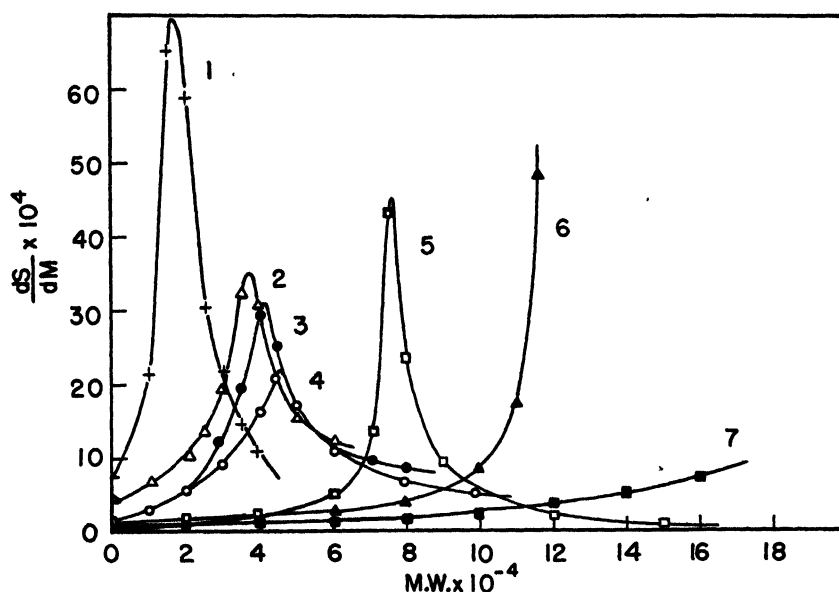


FIG. 2. Differential distribution curves of seven fractions from GR-S sample S-2834.

At first there was good agreement between the value of $X \cdot [\eta]$ from the sum of the various subfractions and that of the original fraction. Towards the end, however, considerable discrepancies were observed owing to removal of high molecular weight material by gel formation.

The data listed in Table VI give an over-all picture of the composition of various solutions used in the refractionation.

Based on the data for all the subfractions (Table VII) an integral distribution curve was drawn, differentiation of which gave the molecular weight distribution curve of Fig. 3.

TABLE VI

COMPOSITION OF MIXTURES FOR THE REFRACTIONATION

Subfraction	Added mixture		Supernatant liquid		T, °C.
	Volume, ml.	C ₆ H ₆ , volume %	Volume, ml.	C ₆ H ₆ , volume %	
<i>Fraction 1</i>					
1 A	—	—	275	71.2	54
1 B	250	73.5	235	73.7	45
1 C	200	75.8	200	76.6	38
1 D	200	76.7	225	77.2	28
<i>Fraction 2</i>					
2 A	—	—	270	71.8	53
2 B	225	74.7	220	74.9	45
2 C	200	76.7	210	77.2	33
2 D	200	76.9	210	77.3	28
<i>Fraction 3</i>					
3 A	—	—	275	73.2	53
3 B	200	74.7	200	74.8	45
3 C	200	76.7	200	77.6	36
3 D	200	77.2	210	78.1	32
3 E	200	77.7	200	78.1	26
<i>Fraction 4</i>					
4 A	—	—	275	75.2	53
4 B	200	76.8	215	76.9	38
4 C	200	77.9	200	78.2	32
4 D	200	78.7	200	79.3	28
<i>Fraction 5</i>					
5 A	—	—	250	75.8	48
5 B	250	78.2	250	78.6	35
5 C	250	79.3	250	79.7	28
5 D	250	79.4	280	80.0	26
<i>Fraction 6</i>					
6 A	—	—	535	75.7	46
6 B	500	77.6	500	77.7	38
6 C	500	78.6	460	78.9	30
6 D	500	79.3	570	79.4	27
<i>Fraction 7</i>					
7 A	—	—	510	77.0	43
7 B	500	78.2	500	78.4	38
7 C	500	78.7	470	78.7	34
7 D	500	79.3	500	79.3	29
7 E	500	80.3	500	80.3	26
<i>Fraction 8</i>					
8 A	—	—	1030	76.8	45
8 B	1000	78.2	1000	78.4	43
8 C	1000	79.1	1040	79.1	40
8 D	1000	80.2	970	80.4	32
8 E	1000	81.0	1225	81.0	27

TABLE VII
INTEGRAL DISTRIBUTION CURVE OF GR-S

Subfraction	Wt. of polymer, gm.	Polymer precipitated, %	Cumulative % "S"	$[\eta]$	$M \times 10^{-4}$
1 A	0.66	4.2	2.1	0.24	0.938
2 A	0.32	2.0	5.2	0.30	1.31
1 B	0.52	3.3	7.9	0.31	1.41
4 A	0.20	1.3	10.2	0.41	2.08
3 A	0.19	1.2	11.5	0.42	2.16
6 A	0.19	1.2	12.7	0.46	2.47
1 C	0.95	6.1	16.3	0.47	2.59
7 A	0.13	0.8	19.8	0.50	2.79
2 B	0.41	2.6	21.5	0.53	3.05
3 B	0.17	1.1	23.4	0.55	3.22
4 B	0.40	2.6	25.2	0.56	3.31
1 D	0.39	2.5	27.7	0.58	3.49
5 A	0.19	1.2	29.9	0.60	3.50
3 C	0.52	3.3	31.4	0.64	4.04
2 C	0.84	5.4	35.8	0.65	4.13
4 C	0.54	3.4	40.1	0.74	5.01
3 D	0.53	3.4	43.6	0.81	5.74
2 D	0.19	1.2	46.0	0.82	5.84
5 B	0.72	4.6	48.8	0.91	6.82
3 E	0.21	1.3	51.9	1.01	7.96
5 C	1.60	10.2	57.6	1.01	7.96
4 D	0.80	5.1	65.4	1.02	8.09
7 B	0.28	1.8	68.7	1.05	8.45
6 C	0.96	6.1	72.6	1.25	10.9
6 D	0.94	6.0	78.8	1.30	11.6
7 C	0.28	1.8	82.7	1.35	12.3
5 D	0.76	4.8	86.0	1.62	16.1
7 D	0.75	4.8	91.0	1.62	16.1
7 E	1.05	6.7	96.6	2.00	22.1
Total	15.67	100.0	100.0		
Original	17.50				

Discussion

Comparison of the above data with those of fractional precipitation for the same polymer and the same pair of liquids (14) shows that both methods lead to essentially the same distribution curve, as it should be. The only significant difference is that, with the present method, separation is much finer for the low than for the high molecular weight material, whereas the reverse is true of fractional precipitation. The same observation was made by Sebrell (17) in the fractionation of Buna-S. This is easily understood from the sequence of operations involved. Scott (16) has shown theoretically that the same molecular weight distribution curves should be obtained by either method. He points out, however, that with fractional solution less low molecular weight material should find its way into the higher molecular weight fractions and concludes that normally extraction should be preferable to precipitation. This is borne out by the present investigation (cf. Fig. 2).

Obviously the "coacervate" method must give the same general results as fractional extraction, with this possible advantage that equilibrium is attained more quickly.

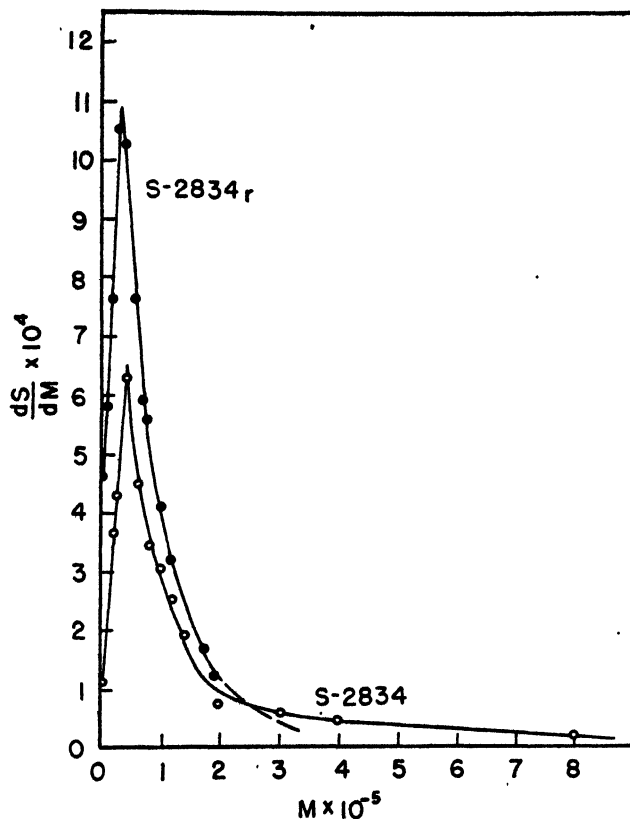


FIG. 3. Differential distribution curve of sample S-2834 compared with the refractionation curve S-2834_r.

Conflicting opinions exist in the literature regarding the "coacervate" method. For instance, workers of the Duclaux group, who originated it, claimed that it was far superior to the usual precipitation. They do admit, however, that they were unable to obtain more than four fractions by the latter method. On the other hand, Morey and Tamblyn (15) tried both methods on a different polymer and found that the fractions were less well separated by extraction from a coacervate. From the present investigation we conclude that the differences between the two methods are more of a practical than of a fundamental character. Also it must be remembered that the distinction between a coacervate and a precipitate is by no means a sharp one; by altering conditions it should be possible to achieve a gradual transition from one form to the other. Thus in the usual precipitation the first fractions certainly are obtained as coacervates. What is in a name?

From the experimental viewpoint the "coacervate" method suffers from a number of limitations. Firstly, because the fractions are obtained as fairly dilute solutions, isolation of the polymer is a complicated problem, as mentioned above. Another consequence of this state of affairs is the greater

number of operations required, which makes the "coacervate" method more time consuming than the conventional ones. Finally, the danger of gel formation is increased by the fact that the high molecular weight material is carried through all the fractionation process and removed only toward the end. This may not be so serious for other types of polymers, but in the case of GR-S it resulted in almost complete loss of the last subfractions in spite of the presence of an antioxidant. Incidentally it also explains why the differential distribution curve obtained by refractionation exhibits a much higher peak at 40,000 than the original one, Fig. 3.

Inspection of Fig. 2 reveals considerable overlapping for fractions 2, 3, and 4. This is easily understood, as it corresponds to the region of molecular weight maximum where the slightest variation in solvent composition entails relatively important changes in the amount of polymer coacervated. That the possibilities of the "coacervate" method were fully exploited is confirmed by the fact that fractionation of both samples gave closely similar results, although considerable experience had been gained in between.

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HYDROGEN EXCHANGE REACTIONS OF PHENOL ETHERS IN ACETIC ACID SOLUTION. PROMOTIVE AND INHIBITORY EFFECTS OF STERIC ORIGIN¹

BY WELDON G. BROWN, KENNETH E. WILZBACH, AND WILBERT H. URRY

Abstract

As a means of avoiding side reactions which were encountered in earlier studies of hydrogen-deuterium exchange of phenol ethers with ethanol-sulphuric acid mixtures, a new procedure has been devised for the study of exchange reactions in acetic acid. The analysis for deuterium in the carboxyl group of acetic acid is performed by adding methyl magnesium iodide solution to the solution of phenol ether in acetic acid, combustion of the methane so produced, and finally, by determining the density of the water formed in the combustion. As compared with the former procedure, which required fractionation of the reaction mixture to recover the pure constituents, advantages in convenience and accuracy are claimed. Results are reported for the following ethers, reacting at 90° C. in the presence of trace quantities of sulphuric acid: anisole, *o*-methylanisole, *m*-methylanisole, 3,5-dimethylanisole, 2-methylcoumarane, veratrole, di-isobutyl catechol ether, and the cyclic mono- (di-, tri-, and tetra) methylene ethers of catechol. The observed variations in rates are interpreted in part according to whether the conditions imposed by structural alterations favor or constrain the formation of an intermediate cation for which a quinoidal configuration of bonds is required. The role of steric factors is most strikingly demonstrated in the series of cyclic ethers of catechol, constraint being evident at a critical ring size (7-membered ring) and largely absent for either smaller or larger rings.

In a previous attempt (10) to demonstrate steric hindrance of hydrogen exchange in di-ortho-substituted phenol ethers difficulties arose because of side reactions in which the aryl groups of the ethers were replaced by ethyl groups derived from the deuterio-ethanol of the medium. The sensitivity of the highly substituted ethers to cleavage in the presence of acids could in itself be regarded as evidence for the existence of an effect closely related to that under investigation, namely, the steric inhibition of resonance, since this effect should render the aryl ether more like an aliphatic ether with respect to acid cleavage. But the occurrence of this reaction vitiated the observations on hydrogen exchange because the free phenols thereby formed are theoretically not susceptible to steric hindrance and in any case would undergo exchange of nuclear hydrogens much more rapidly than the ethers.

The complications arising from the use of ethanol are avoided by the use of carboxyl-labeled deuterio-acetic acid which also fulfills the requirements for a medium containing active deuterium in which the phenol ethers will be soluble. In this medium the phenol ethers, together with the necessary catalytic quantities of sulphuric acid, could be heated for long periods of time with no indications of side reactions of any kind with one exception to be noted later.

The adoption of acetic acid necessitated an extensive revision of the experimental technique formerly employed since it was no longer feasible to recover

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Contribution from the George Herbert Jones Laboratory of the University of Chicago, Chicago, Illinois.

the pure constituents from the reaction mixtures by fractional distillation. In the procedure eventually developed no separation of any kind is performed. Methyl magnesium iodide is added to the reaction mixture forming methane by reaction with the acetic acid. The methane is freed from organic impurities, burned, and analyzed for deuterium on the basis of the density of the water of combustion. It is found that no isotopic discrimination occurs in the reaction of methyl magnesium iodide with deuterated acetic acid; the method is therefore not subject to errors which may arise from isotopic separation as in fractional distillation (11).

In pursuance of the steric aspects of the phenol ether exchange reactions, the emphasis has shifted from a study of the steric effects resulting from ortho substituents, which can only be negative (inhibitory), to a study of the consequences of ring closure and ring size in bicyclic ethers which can produce either positive (promotive) or negative steric effects. It is hoped thereby to minimize the ambiguity inherent in the elucidation of the steric factor associated with the introduction of substituent groups which arises from the fact that electronic activation, or deactivation, by the groups is invariably superimposed.

The basis for the prediction of steric effects lies in the mechanism assumed for the acid-catalyzed exchange of ortho and para hydrogen atoms of the phenol ethers. It is assumed, largely on the basis of the analogous reactions of aromatic amines which have been studied exhaustively (2, 3), that the exchange is initiated by transfer of deuterium from the acid to an ortho or para carbon atom. The intermediate cation, whether it be an activated complex or a chemical species of finite lifetime, must possess a quinoidal bond arrangement and, for lowest energy, the plane defined by the oxygen atom (now an oxonium oxygen) and the two carbon atoms to which it is bound must coincide with the plane of the quinoid ring. An inhibitory steric effect is to be expected if for any reason the most favorable configuration cannot be attained. This might be the result of interfering substituents occupying both ortho positions, or of a bicyclic structure having a rigid and noncoplanar configuration. If the structure is such that the key atoms are automatically fixed in a suitable configuration, as in planar bicyclic ethers, then by comparison with analogous open-chain structures, a promotive steric effect may be expected. Promotive steric effects cannot be large. The open-chain structure which serves to define such an effect is presumably free to attain the favorable configuration; the difference, if any, must arise from the entropy decrease associated with the conversion of the open-chain molecule to a quinoidal intermediate which has a relatively more fixed structure. These different situations have all been encountered in the series of aromatic amines previously investigated and as a consequence the conditions necessary for steric effects in the phenol ethers can be set forth with considerable confidence.

The mechanism outlined above for the hydrogen exchange reactions, and the assumption that only ortho and para hydrogen atoms exchange under mild conditions, derive support from the following observations. Anisole,

which did not exchange hydrogen with acetic acid alone at 90° C. in 48 hr., reacted slowly in the presence of sulphuric acid (mixture contained 0.88 mole % sulphuric acid), reaching a value just short of three for the number of hydrogen atoms participating in the same period of time. With the introduction of methyl groups in the meta position, the rate of the sulphuric acid catalyzed reactions became too fast for measurement; the equilibrium attained in the partition of deuterium clearly indicated three exchangeable hydrogen atoms in *m*-methylanisole and in 3,5-dimethylanisole. These ethers were sufficiently reactive to undergo exchange at a measurable rate in the absence of sulphuric acid. The activating effect of substituent methyl groups thus demonstrated is the normal effect for a nuclear substitution reaction initiated by an electrophilic reagent.

An activating effect of smaller magnitude, due to alkyl groups in the ortho position, is indicated by the higher initial rates of exchange of *o*-methylanisole and 2-methylcoumarane, as compared with anisole. That the curve for anisole eventually crosses the others is a consequence of its having three active hydrogens whereas the others have two. The bicyclic ether, 2-methylcoumarane, having a 5-membered ring which is doubtless coplanar with the benzene ring, exchanges at a rate significantly higher than that of *o*-methylanisole. This difference is viewed as an example of a promotive steric effect.

For the further studies of ring structures in relation to steric effects, the polymethylene ethers of catechol were selected, largely for the reason that these compounds are readily accessible. It is assumed that each oxygen should activate hydrogen atoms ortho and para to it and consequently that there should be four exchangeable hydrogen atoms. Since the activation effects do not overlap, to a first approximation, the general level of reactivity should be comparable with that of anisole except to the extent that it may be modified by steric effects. None of our experiments were of sufficiently long duration to demonstrate the presence of four active hydrogens but the initial rates did indeed fall in a conveniently measurable range.

In the series, $C_6H_4O_2(CH_2)_x$, for values of x ranging from one to four, we pass through a number of characteristically different steric situations without at the same time altering the number or the essential character of the substituents on the benzene ring. The significant features of each situation are indicated in Fig. 1; with these are to be correlated the variations in rate of hydrogen exchange. A small decrease in rate is noted on progressing from $x = 1$ to $x = 2$; a further and larger decrease is seen at $x = 3$, while at $x = 4$ the reactivity returns abruptly to approximately the original level. The inhibitory steric effect associated with the 7-membered ring ($x = 3$) is not new, the counterpart having been previously observed (3) in a series of bicyclic amines. However, this is the first demonstration that the greater flexibility of the 8-membered ring permits a return to normal reactivity.

Up to this point the experimental observations are in highly satisfactory agreement with theory, but when a comparison is made of the cyclic catecho ethers with open-chain ethers the agreement ends. Whereas catecholl

methylene ether should be equal in reactivity with veratrole, or possibly higher because of the promotive steric effect of the 5-membered ring, the observed reactivity in hydrogen exchange is actually lower. This result is

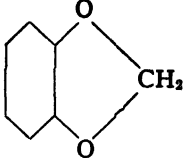
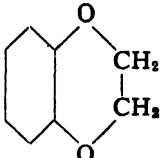
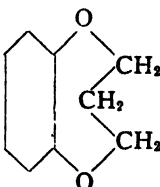
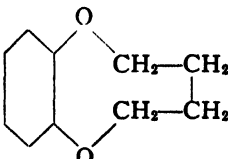
		Configuration of α -carbon atoms	n' , at 12 hr.
Methylene ether ($x = 1$)		Fixed in plane of benzene ring.	1.30
Ethylene ether ($x = 2$)		Probably out of plane, but oscillation through plane possible.	0.79
Trimethylene ether ($x = 3$)		Out of plane; semirigid structure.	0.23
Tetramethylene ether ($x = 4$)		Position in plane possible.	0.93

FIG. 1. Steric relationships in cyclic ethers of catechol.

especially puzzling in view of the claim (1), based on other chemical evidence, that "the benzenoid ring of methylenedioxybenzene is more reactive than that of veratrole." The chemical evidence to which reference is made is not altogether convincing but the conclusion as stated is of course compatible with theory. That the anomaly in hydrogen exchange is not confined to veratrole is shown by the fact that the diisobutyl ether of catechol exchanges at a rate very nearly equal to that of veratrole.

It must be admitted that catechol methylene ether offered greater difficulties in the measurement of hydrogen exchange than any other compound examined. Except when the most extreme precautions were taken to degas the materials and to exclude air, the reaction mixtures darkened and positive ferric chloride tests were observed, indicating cleavage. The results of such experiments were low, possibly because of consumption of sulphuric acid by reaction with cleavage products. In the final experiments, furnishing the

results here reported, the mixture at five hours was colorless and gave a negative ferric chloride test; at 12 hr. a slight coloration had become evident and a faint ferric chloride test was obtained. The reliability of these results is probably less than for any other results given, but at the same time the uncertainty is believed to be small in comparison with the magnitude of the anomaly under consideration.

In this discussion the role of steric inhibition of resonance in hydrogen exchange reactions has been ignored. It will be obvious that we cannot have steric hindrance in an assumed quinoidal intermediate cation without at the same time subjecting the ether from which the cation is formed to steric inhibition of resonance. In a chemical reaction of this kind the two effects must operate simultaneously. On energetic grounds it may be reasoned that strain in the quinoidal intermediate will be more crucial than a corresponding degree of strain in one of the resonance forms of the ether. For this reason it seems desirable to consider steric effects in reactivity principally in terms of the stability of the reaction intermediate.

Experimental

General Procedure

For each substance investigated, a number of tubes were prepared, each containing 0.007 mole of the substance and 2 ml. of a stock solution made by adding 1 ml. of sulphuric acid to 100 ml. of acetic acid. Each tube, after filling, was attached to a vacuum line and air was removed by repeated freezing, pumping, and melting operations, and was then sealed under vacuum. The tubes were placed in a thermostat at $90 \pm 0.1^\circ$ for various reaction periods.

As each tube was opened, a test for phenols was made using ferric chloride solution. This test was negative for all substances studied except catechol methylene ether, the behavior of which has been noted earlier. The mixtures were then analyzed for their acidic deuterium content by the method to be described later.

A control experiment was carried out for each substance in which a similar mixture, with no sulphuric acid present, was heated for an extended period. With the majority of ethers, no exchange occurred under these conditions. Exchange was observed with *m*-methylanisole and 3,5-dimethylanisole to the extent shown in Table I.

The extent of hydrogen exchange is expressed in terms of a quantity, n' , which is given by

$$n' = \frac{N_A}{N_S} \left[\frac{D^0 - D}{D} \right],$$

where N_A/N_S is the molar ratio of acetic acid to solute, D^0 is the initial concentration and D the final concentration of deuterium in the acetic acid. The quantity, n' , is related to the true number of hydrogen atoms exchanging per mole of solute, n , by a partition coefficient, p , such that $n' = np$, and p

TABLE I

HYDROGEN EXCHANGE OF PHENOL ETHERS WITH ACETIC ACID AT 90° C.

Ether	Hours	D ₂ O, %		n'
		Initial	Final	
Anisole	2.0	2.40	2.13	0.63
	6.0	2.40	1.96	1.11
	12.0	2.40	1.83	1.54
	46.7	2.40	1.65	2.42
o-Methylanisole	2.0	2.40	2.04	0.87
	12.0	2.40	1.87	1.41
2-Methylcoumarane	2.0	2.40	1.98	1.05
	4.0	2.40	1.93	1.21
	18.0	2.40	1.85	1.47
m-Methylanisole	2.0	2.40	1.57	2.62
	46.0	2.40	1.57	2.62
Same, no sulphuric acid added	50.0	2.61	1.99	1.57
3,5-Dimethylanisole	0.25	2.40	1.61	2.42
	0.5	2.46	1.57	2.80
	12.0	2.46	1.57	2.80
	24.0	2.46	1.58	2.76
Same, no sulphuric acid added	0.25	2.50	1.94	1.43
	1.0	2.50	1.79	1.99
	25.5	2.50	1.66	2.54
Veratrole	12.0	2.46	1.82	1.73
	24.0	2.46	1.68	2.30
	48.0	2.46	1.56	2.85
	90.0	2.46	1.56	2.85
Catechol diisobutyl ether	6.0	2.46	1.98	1.20
	12.0	2.46	1.84	1.67
	24.0	2.46	1.72	2.13
	48.0	2.46	1.56	2.85
Catechol methylene ether	5.2	2.46	2.18	0.64
	12.0	2.46	1.95	1.30
Catechol ethylene ether	6.0	2.46	2.19	0.61
	12.0	2.46	2.12	0.79
	24.0	2.46	1.98	1.17
	48.0	2.46	1.81	1.70
	120.0	2.46	1.64	2.48
Catechol trimethylene ether	6.0	2.46	2.39	0.14
	12.0	2.46	2.35	0.23
	24.0	2.46	2.18	0.61
	48.0	2.46	2.03	1.00
	156.5	2.46	1.82	1.49
Catechol tetramethylene ether	6.0	2.40	2.14	0.60
	12.0	2.40	2.02	0.93
	24.0	2.40	1.87	1.40

* The results given are for the sulphuric acid catalyzed reactions, except as otherwise noted.

has values in the neighborhood of 0.8 for solutes of the type under consideration. This relationship applies only to equilibrium conditions of course; for intermediate degrees of reaction the meaning of n' is somewhat fictitious but it serves as a convenient measure.

Deutero-acetic Acid

Acetic acid containing approximately 10% CH_3COOD was prepared in order that methane produced by its reaction with methyl magnesium iodide would burn to yield water in the upper range of calibration of the quartz float (0 to 3 mole % D_2O). Deuterium oxide, 2 gm., was heated under reflux with 20 gm. of acetic anhydride for 10 hr. Then, 108 gm. of pure acetic acid was added and the mixture was purified by fractional distillation through a 15-plate, all-glass column.

In the absence of added sulphuric acid no measurable exchange of hydrogen between the methyl groups and the carboxyl groups of acetic acid could be observed after 618 hr. at 90°C . With sulphuric acid, at the concentration employed in the ether exchange experiments, this exchange reached 2% of completion after 188 hr. at 90°C . and is thus negligible for the shorter periods of the ether exchange reactions.

Deuterium Analyses

The apparatus used in the determinations is shown in Fig. 2.

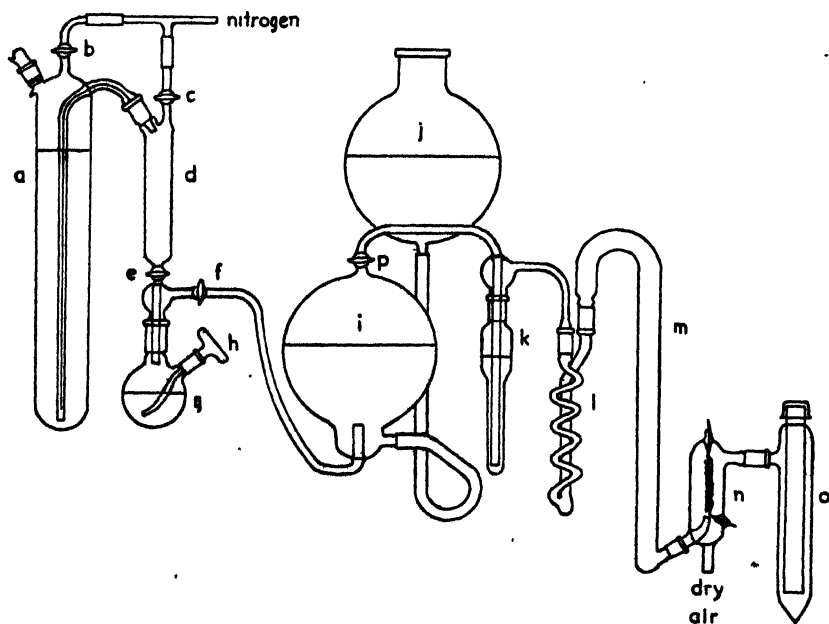


FIG. 2.

Before performing an analysis, the leveling flask (*j*) was placed below the gas receiver (*i*), and stopcocks (*c*), (*e*), and (*f*) were opened to allow a slow stream of nitrogen to pass through the apparatus into the gas receiver. While

the dry nitrogen was passing through it, the reaction flask (*g*) was dried by heating with a gas flame. After 1.5 liters of nitrogen had collected in the gas receiver, the flow of nitrogen was stopped by closing stopcocks (*c*), (*e*), and (*f*). The leveling flask was then placed above the gas receiver, and the stopcock (*p*) was opened to allow the nitrogen to sweep the purification train and combustion chamber to remove residual methane from the previous determination. This sweeping with nitrogen was repeated three times.

Next, the stopper (*h*) was removed from the reaction flask (*g*), and pure di-*n*-butyl ether (15 ml.) and the sample to be analyzed (2 ml.) were introduced. The leveling flask was placed below the gas receiver, stopcocks (*b*), (*e*), and (*f*) were opened and a positive nitrogen pressure forced the Grignard reagent from its storage vessel (*a*) into the reaction flask. The rate of addition of the methyl magnesium iodide solution was regulated by adjusting stopcock (*e*). During the addition of the Grignard reagent, magnesium salts precipitated as a spongy mass. It was necessary, therefore, to stir the reaction mixture with the stirring rod attached to the stopper (*h*). The methane (about 800 ml.) was collected in the gas receiver.

When methane evolution had stopped, stopcocks (*b*), (*e*), and (*f*) were closed. The leveling bulb was placed above the gas receiver, and the stopcock (*p*) was adjusted to allow a gas flow of about 30 ml. per minute. The methane bubbled through the trap (*k*) containing alcoholic silver nitrate to remove traces of methyl iodide. Alcohol and water vapor remaining in the gas were removed by the cold trap (*l*), immersed in a dry ice - acetone bath, and the drying tube (*m*), packed with indicating Drierite and phosphorus pentoxide on glass beads.

In the combustion chamber (*n*), the methane was burned in a stream of dry air on a glowing platinum wire. Water resulting from the combustion was condensed in the cold trap (*o*). This water, after one vacuum distillation, was sufficiently pure for analysis. The deuterium content was determined using the temperature-float method previously described (7).

The Grignard reagent, 2 *N* methyl magnesium iodide in butyl ether, was prepared in an atmosphere of nitrogen from 200 gm. of methyl iodide, 34 gm. of magnesium turnings, and 350 ml. of di-*n*-butyl ether. After the mixture had been held at 35° C. for two hours, the pressure was lowered to 15 mm. to remove unreacted methyl iodide. The Grignard reagent was then filtered through glass wool and stored under nitrogen in a dark vessel.

Five determinations, at intervals over a period of two months, on the same lot of deuterio-acetic acid furnished the following results, expressed in terms of % D₂O in the water of combustion: 2.47, 2.46, 2.47, 2.46, 2.46.

That the Grignard reagent did not react preferentially with either isotopic form of acetic acid is shown by the analysis of three successive samples of methane gas generated from one sample of acetic acid: 2.75, 2.74, 2.75.

Preparation of Aryl Ethers

The liquid ethers used in this work were carefully distilled through an efficient column and then molecularly distilled immediately before use. The physical constants are given in Table II.

TABLE II
PHYSICAL CONSTANTS OF THE PHENOL ETHERS

Compound	B.p., ° C.	n_D^{20}	d_{20}^{20}
Anisole	155 (750 mm.)	1.5152	0.9910
<i>o</i> -Methylanisole	71 (23 mm.)	1.5164	0.9851
<i>m</i> -Methylanisole	73 (23 mm.)	1.5119	0.9766
3,5-Dimethylanisole	89 (15 mm.)	1.5110	0.9569
2-Methylcoumarane	92 (23 mm.)	1.5286	1.0320
Veratrole	92 (12 mm.)	1.5339	1.0828
Catechol diisobutyl ether	135 (11 mm.)	1.4870	0.9406
Catechol methylene ether	57.2 (11 mm.)	1.5382	1.0640
Catechol ethylene ether	92 (11 mm.)	1.5500	1.1685
Catechol trimethylene ether	94 (8 mm.)	1.5430	1.1351
Catechol tetramethylene ether	113 (14 mm.)	1.5407	1.1103

Veratrole was prepared by the addition of aqueous potassium hydroxide to a cooled solution of catechol and dimethyl sulphate in methanol (9).

Catechol methylene ether was prepared from catechol, sodium, and methylene chloride by the method of Robinson and Thomas (8).

Catechol ethylene ether was prepared by heating a mixture of catechol, ethylene bromide, potassium carbonate, and copper powder (5).

Catechol trimethylene ether was prepared by the reaction of trimethylene bromide with a solution of catechol and sodium methylate in anhydrous methanol (12).

Catechol tetramethylene ether was prepared by the addition of ω -bromobutyl catechol ether to a hot mixture of potassium carbonate in amyl alcohol (13).

Catechol diisobutyl ether was made by the reaction of isobutyl bromide with the sodium salt of catechol in isobutyl alcohol.

Anisole, *o*-methylanisole, *m*-methylanisole, and 3,5-dimethylanisole were obtained by the action of sodium hydroxide and dimethyl sulphate on the respective phenols (6).

2-Methylcoumarane was obtained from *o*-allylphenol by heating with a mixture of acetic acid and hydrogen bromide (4).

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NOTICE

THE AUTHOR AND SUBJECT INDEXES FOR EACH OF THE SECTIONS, A, B, C, D, E, AND F, OF THE CANADIAN JOURNAL OF RESEARCH FOR THE YEAR 1949 WILL BE ISSUED WITH AN EARLY NUMBER OF THE SECTION IN 1950.

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A NOTE ON THE EFFECT OF PHOSGENE UPON THE INFLAMMABILITY LIMITS OF HEXANE¹

BY K. J. MCCALLUM AND HELEN M. TRAINOR

Abstract

The inflammability limits of mixtures of phosgene and hexane in air at approximately atmospheric pressure have been investigated. The addition of phosgene causes the upper and lower inflammability limits of hexane to approach each other until they meet at a composition containing 3.4 volume % hexane and 19.1 volume % phosgene.

Introduction

The upper and lower inflammability limits of hexane in air have been reported to be 6.9 and 1.4 volume % (4) and 6.9 and 1.2 volume % (1). This paper reports the effects of the addition of phosgene upon these limits.

Materials and Procedure

The phosgene was of commercial grade and was used as received with no further purification. The material was analyzed by the method of Nenitzescu and Pana (5) to determine the percentage of free chlorine. This was found to be 0.46%. No attempt was made to determine carbon monoxide or other gases.

The hexane used was Eastman Kodak Company's hexane from petroleum. The value of the refractive index at 20° C., using the sodium D line, was 1.37576 as compared to the value of 1.37506 given by Egloff (2).

The inflammability limits of mixtures of phosgene, hexane, and air were determined at room temperature and approximately 1 atm. pressure. The inflammability tests were made in a Pyrex tube, 47.5 mm. inside diameter and 103 cm. long. The method of preparing and mixing the gases of different compositions was the same as that previously described (4). A small gas flame was used as the source of ignition. All observations were made with upward propagation of the flame and with the lower end of the tube open, so that the pressure during the combustion remained close to the atmospheric pressure. Gases of various compositions were tested until compositions were found that were approximately 0.3% on either side of a limit mixture.

¹ Manuscript received January 10, 1949.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

Results and Discussion

In Table I are given the compositions of limit mixtures of phosgene, hexane, and air. The table contains the partial pressures of the gases in the mixtures between which the limits were found to lie. The compositions of the limit mixtures in volume per cent were calculated on the assumption that partial pressure per cent is equal to volume per cent.

TABLE I
INFLAMMABILITY LIMITS FOR PHOSGENE-HEXANE-AIR

Partial pressure of limit mixture, mm. mercury		Barometer height, mm. mercury	Vol. % hexane (mean)	Vol. % phosgene (mean)	Vol. % air (mean)
Hexane	Phosgene				
10.2-10.7	0	705.5	1.5	0	98.5
52 -54	0	709.0	7.5	0	92.5
14.2	46 - 48	710.8	2.0	6.55	91.45
43.0-44.2	43.0- 44.2	715.0	6.1	6.1	87.8
29.6-29.5	115.9-111.9	719.2	4.1	15.8	80.1
15.4-18.4	86.4- 86.0	718.5	2.35	12.0	85.65
24.0-22.8	136.8-137.0	718.5	3.26	19.0	77.74
34.3-37.5	79.3- 79.5	718.5	5.10	11.0	83.9
21.8-24.0	133 -135	718.5	3.20	18.6	78.2
24.0-24.5	136.8-138.2	718.5	3.37	19.1	77.53
26.6	129	718.5	3.70	18.0	78.3

The upper and lower inflammability limits of hexane in air were found to be 7.5 volume % and 1.5 volume %, respectively. The corresponding values reported by McCallum and Graham (4) are 6.9% and 1.4%, respectively, while Coward and Jones (1) report 6.9% and 1.2% for *n*-hexane. The agreement is within the precision of these experiments.

In Fig. 1, the inflammability limits for this system are plotted as volume per cent phosgene against volume per cent hexane. The addition of phosgene to hexane is seen to bring the upper and lower inflammability limits together until eventually they meet, the maximum in the curve occurring at a composition containing 3.4 volume % hexane and 19.1 volume % phosgene.

By combining the data for this system with those for the systems hydrogen cyanide-phosgene-air and hydrogen cyanide-hexane-air (4), the inflammability limits in the quaternary system hydrogen cyanide-hexane-phosgene-air can be calculated assuming that the law of Le Chatelier (3) holds. This law, which has been found to hold in the system hydrogen cyanide-hexane-air, states that mixing two upper or two lower binary limit mixtures will produce an upper or lower limit mixture, respectively, of the resulting ternary system.

The essential assumption is, that just as the law gives the inflammability limits of mixtures of the two inflammable gases, hydrogen cyanide and hexane,

in air, it also gives the limits of mixtures of these gases in a given phosgene-air mixture. The upper and lower inflammability limits of hexane and of hydrogen cyanide, separately, in a mixture containing phosgene and air in a

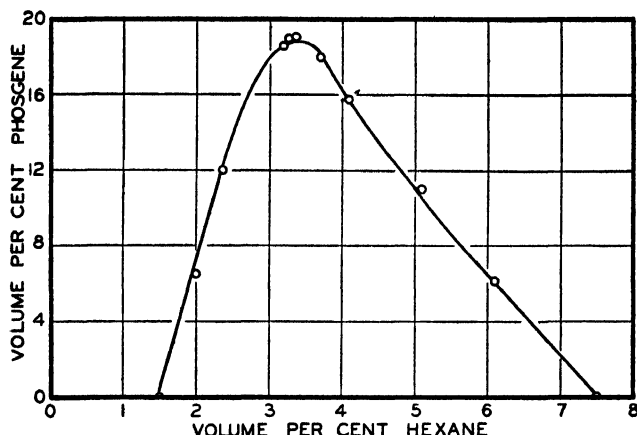


FIG. 1. *Inflammability limits in the system phosgene-hexane-air.*

given ratio, can be obtained from the curves for the systems hydrogen cyanide-phosgene-air, and hexane-phosgene-air. Those compositions of hexane and hydrogen cyanide together in this phosgene-air mixture which are inflammable can be found by joining the points representing these upper and lower limits, respectively, on a plot of volume per cent hexane versus volume per cent hydrogen cyanide. The inflammable region then constitutes a band across the figure. Such a diagram can be drawn for various phosgene-air ratios. Since the effect of phosgene on both hydrogen cyanide and hexane is to bring the upper and lower limits closer together, the band becomes narrower with increasing values of the phosgene-air ratio, until it disappears at a value of the ratio equal to 0.247. No mixture of hydrogen cyanide, hexane, phosgene, and air would be inflammable in which the ratio of phosgene to air is greater than this value.

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A NOTE ON THE EFFECT OF CARBON DIOXIDE UPON THE INFLAMMABILITY LIMITS OF HYDROGEN CYANIDE¹

BY K. J. MCCALLUM AND HELEN M. TRAINOR

Abstract

The inflammability limits of mixtures of carbon dioxide and hydrogen cyanide in air have been investigated. The effect of the addition of carbon dioxide is to bring the upper and lower inflammability limits of hydrogen cyanide together, until they meet at a composition containing 36 volume per cent carbon dioxide and 12 volume per cent hydrogen cyanide.

Introduction

In a previous paper (2) the effect of the vapors of cyanogen chloride, phosgene, chloroform, hexane, heptane, and methyl chloroformate upon the inflammability limits of hydrogen cyanide in air was reported. This note reports the effect of carbon dioxide upon these limits.

Materials and Procedure

Commercial grade liquid hydrogen cyanide was dried with anhydrous calcium chloride. Successive fractions of the vapor were condensed and analyzed by the method previously described. The experimental values found were 100.4% hydrogen cyanide on all fractions.

The carbon dioxide was obtained from the sublimation of dry ice. The gas was analyzed by absorbing a measured volume in potassium hydroxide solution. The residual unabsorbable gas was 0.1% by volume.

The gas mixtures were tested for inflammability in a Pyrex tube 47.5 mm. inside diameter and 103 cm. long. The procedure used in preparing the gas mixture was the same as that previously described (2). All observations were made with upward propagation of the flame and with the lower end of the tube open to the atmosphere. A small gas flame was used as the source of ignition.

Various mixtures of gases were tested until compositions were found that were approximately 0.5% on either side of a limit mixture.

Results and Discussion

In Table I are given the inflammability limits on mixtures of hydrogen cyanide, carbon dioxide, and air. In the first two columns are given the partial pressures of hydrogen cyanide and carbon dioxide between which the limits were found to lie. The compositions of the limit mixtures in volume per cent, given in the last three columns, were calculated on the assumption that partial pressure per cent is equal to volume per cent for these mixtures.

¹ Manuscript received January 10, 1949.

Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

TABLE I

INFLAMMABILITY LIMITS FOR HYDROGEN CYANIDE - CARBON DIOXIDE - AIR

Partial pressure of limit mixtures, mm. mercury		Barometer height, mm. mercury	Vol. % HCN (mean)	Vol. % CO ₂ (mean)	Vol. % air (mean)
HCN	CO ₂				
97.0- 97.5	242 -246	712.5	13.62	34.25	52.13
87.3- 87.8	255 -258	712.5	12.29	36.00	51.71
60.9- 65.2	71.8- 72.0	718.8	8.77	10.01	81.22
111 -115	225.7-226.4	717.2	15.76	31.52	52.72
84.6- 84.9	256.3-260.1	717.2	11.80	36.00	52.20
180.0-180.4	130.0-134.7	720.0	25.05	18.40	56.55
235.2-236.0	65.0- 68.7	723.8	32.50	9.25	58.25
91.1- 91.8	257.5-259.1	720.0	12.70	35.90	51.40
142.3-142.7	177.1-185.2	712.5	20.00	25.48	54.52
60.5- 64.6	141.5-142.0	712.5	8.76	19.88	71.36
78.7- 81.1	249.4-250.0	712.5	11.20	35.00	53.80
72.9- 76.0	216.8-217.5	723.4	10.28	30.00	59.72
75.3- 77.5	234.0-236.8	714.3	10.72	33.00	56.28

The plot of the results in Fig. 1 shows that the addition of carbon dioxide causes a rise in the lower inflammability limit and a decrease in the upper inflammability limit until the limits coincide, the maximum in the curve

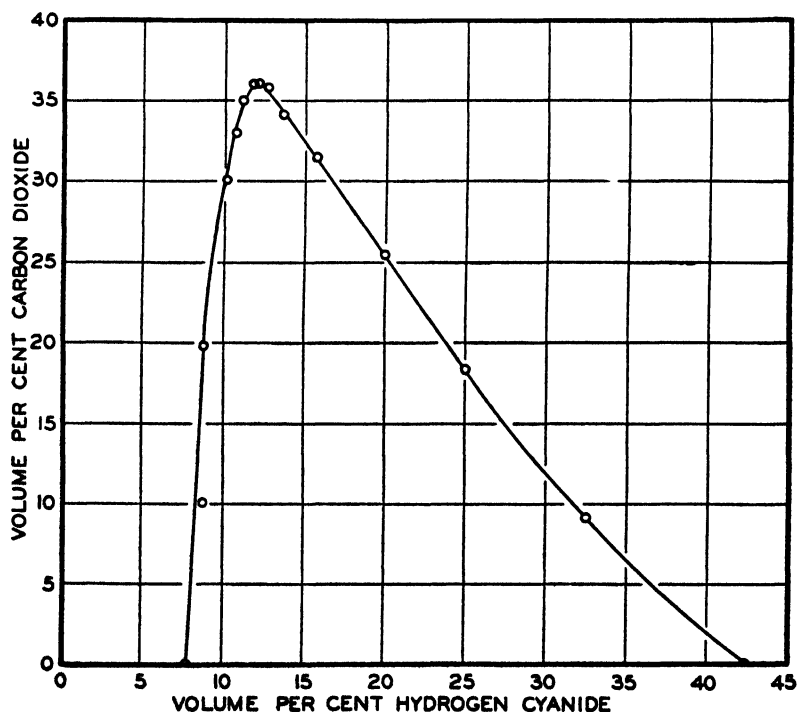


FIG. 1. Inflammability limits in the system carbon dioxide - hydrogen cyanide - air.

occurring at 36 volume % carbon dioxide and 12 volume % hydrogen cyanide. Although the maximum in the curve for the system hydrogen cyanide – cyanogen chloride – air occurs at nearly the same position (36 volume % cyanogen chloride and 12 volume % hydrogen cyanide) (2), the effect of the addition of cyanogen chloride differs from that of carbon dioxide in that small amounts of cyanogen chloride cause an initial decrease in the lower inflammability limit of hydrogen cyanide.

The volume per cents of added vapor at the maximum of the inflammability curves for hydrogen cyanide with added phosgene and chloroform are 15% and 16%, respectively (2), definitely lower than the values for added carbon dioxide and cyanogen chloride. These results are in qualitative agreement with the observation (1) that the heat capacity of the added vapor may be one factor in determining its effect upon the inflammability.

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RELATIVE REACTIVITIES OF THE GEOMETRICAL ISOMERS OF HEXACHLOROCYCLOHEXANE¹

BY D. J. WHITTINGHAM² AND D. L. GARMAISE

Abstract

The dehydrochlorination of hexachlorocyclohexane to trichlorobenzene in an alcoholic solution of piperidine was investigated, and the relative reactivities of four geometrical isomers of hexachlorocyclohexane determined. Activation energies and *PZ* values for the alpha, gamma, and delta isomers were obtained; the beta isomer reacted too slowly under the conditions used for convenient rate studies to be made. The order of reactivity was found to be alpha, delta > gamma >> beta; the order of reactivity is interpreted on the basis of differing degrees of steric hindrance in the isomers.

Introduction

The discovery in 1942 of the insecticidal properties of the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane led to a renewed interest in the geometrical isomerism of this compound. It was first prepared in 1825 by Faraday (4) by bubbling chlorine into benzene in the sunlight; the existence of more than one isomer was recognized in 1884 by Schüpphaus (8) through observation of two crystal forms. Van der Linden (7) in 1912 succeeded in isolating four isomers, named alpha, beta, gamma, and delta, with widely different melting points and solubilities. Recently the isolation of a new isomer was reported by Kauer, DuVall, and Alquist (6). Hassel and Kringstad (5) have proposed that cyclohexane exists only in the chair, or "Z" form; if this is true for hexachlorocyclohexane, then eight geometrical isomers are theoretically possible, of which one is molecularly asymmetric.

Of the known isomers, it soon appeared evident that the beta isomer, the highest melting and most stable, had an alternating up and down arrangement of chlorines, which leads to the creation of an almost planar ring of chlorine atoms, known as the "beta ring", encircling the carbons (3). The other isomers then have one or more chlorines displaced outside of the beta ring.

The purpose of this work was to determine the relative ease of dehydrochlorination of the then known isomers (this work was undertaken before the isolation of the epsilon isomer) as an aid in proof of structure, and to test the proposal that insecticidal activity is associated with ease of dehydrochlorination.

Preparation and Separation of the Isomers

Chlorine was passed through distilled water and concentrated sulphuric acid, into a 1 liter flask containing 300 gm. of dry benzene, for 23 hr. at 20° C. The reaction mixture was irradiated by a mercury discharge lamp.

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Contribution from the Chemical Laboratories of the University of New Brunswick, Fredericton, N.B.

² Now at University College, London.

The crude product (166 gm.) was then fractionally crystallized using a variety of solvents, following the procedure given by Smart (9). The amounts of isomers obtained pure were:

Alpha	102.0 gm., m.p. 157 to 157.5° C.
Beta	5.1 gm., m.p. 308 to 309° C.
Gamma	16.0 gm., m.p. 112 to 112.5° C.
Delta	2.9 gm., m.p. 138 to 139° C.

Melting points are corrected.

The reaction studied was the known conversion of hexachlorocyclohexane to a mixture of trichlorobenzenes using an alkaline reagent dissolved in alcohol. Preliminary trials indicated that potassium hydroxide caused too fast, and pyridine too slow, a reaction for convenient rate studies; the secondary amine, piperidine was adopted as the most convenient alkaline reagent.

The standard experimental procedure was to dissolve 0.3623 gm. (1.25×10^{-3} mole) of the hexachlorocyclohexane isomer in 95% ethyl alcohol and add 50.00 ml. of 0.0747 *N* alcoholic piperidine solution (3.74×10^{-3} mole), and to add further ethyl alcohol to bring the volume to 100.0 ml. The reaction solution was contained in an 8 in. test tube held by a stopper in a 1 liter three-necked flask, which served as a constant temperature vapor bath. Various solvents were refluxed in the flask to give the desired reaction temperatures. At intervals, 10.00 ml. aliquots were removed with a calibrated pipette, added to 50 ml. of water to quench the reaction, and the unreacted piperidine titrated with standard hydrochloric acid solution, using the mixed indicator bromcresol green - methyl red (3 : 2). The extent of reaction for a given time interval was calculated on the basis of the equation



Fig. 1 shows the rate of dehydrochlorination of the alpha isomer at various temperatures.

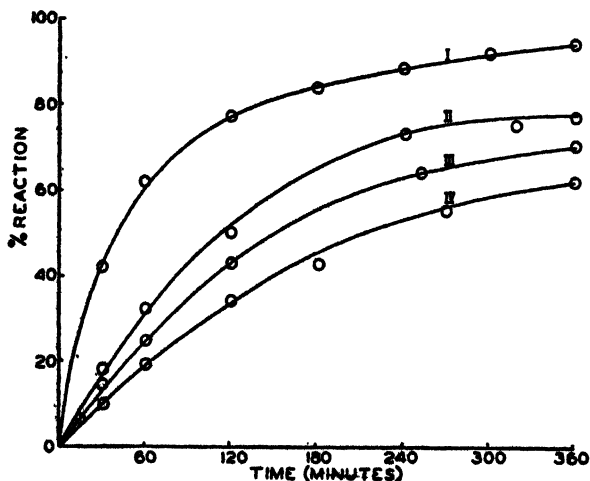


FIG. 1. Dehydrochlorination of the alpha isomer at various temperatures. Initial concentration of alpha isomer = 0.0125 mole per liter.
I, 79.5° C.; II, 65.0; III, 61.5; IV, 56.2.

Analogous families of curves were obtained with the gamma and delta isomers; with the beta isomer the rate was so slow under these conditions that good results could not be obtained. Only 15% of the beta isomer had reacted after seven days at 79.5° C.

The reaction was shown to follow a second-order equation for the alpha, gamma, and delta isomers; straight line relations between time of reaction and $\frac{x}{a-x}$ were obtained (Figs. 2, 3, and 4), where

x = moles of hexachlorocyclohexane isomer which react in time t ,

a = moles of isomer originally present.

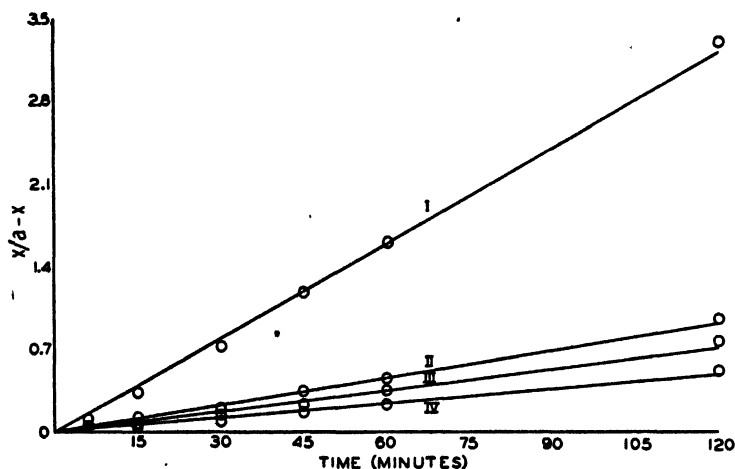


FIG. 2. Determination of second-order rate constants for the alpha isomer at various temperatures. $a = 0.0125$ mole per liter.
I, 79.5° C.; II, 65.0; III, 61.5; IV, 56.2.

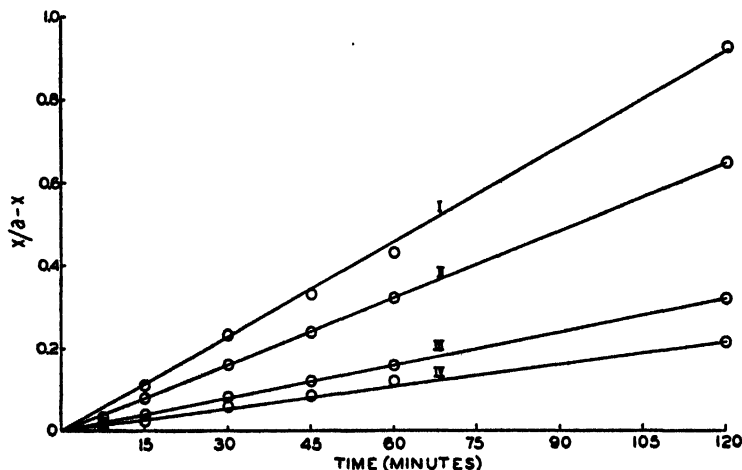


FIG. 3. Determination of second-order rate constant for the gamma isomer at various temperatures. $a = 0.0125$ mole per liter.
I, 79.5° C.; II, 72.0; III, 61.5; IV, 56.2.

The data on the rate of reaction of the beta isomer were inadequate for other than qualitative comparison.

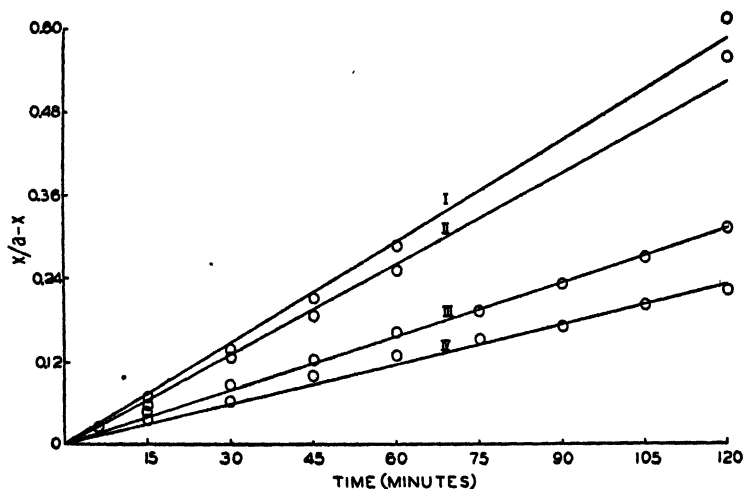


FIG. 4. Determination of second-order rate constants for the delta isomer at various temperatures.

I	79.5° C.	$a = 0.00230$ mole per liter.
II	72.0	$a = 0.00384$ mole per liter.
III	61.5	$a = 0.00767$ mole per liter.
IV	56.2	$a = 0.00767$ mole per liter.

The second-order rate constants obtained from the above data are listed in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS OF THE ISOMERS AT VARIOUS TEMPERATURES

Temperature, °C.	k , liters/mole/sec.		
	Alpha $\times 10^3$	Gamma $\times 10^3$	Delta $\times 10^3$
79.5	12.5	3.4	11.9
72.0		2.6	6.4
65.0	3.8		
61.5	2.7	1.2	1.9
56.2	2.0	0.92	1.3

For the beta isomer; at 79.5° C., " k " is roughly 10^{-6} .

These values of k were plotted in the graph $\log k$ against $\frac{1}{T}$ (Fig. 5) to obtain activation energies and the values of the PZ factor in the Arrhenius equation.

From this graph, the values for E and PZ listed in Table II were obtained.

Discussion

The great resistance to dehydrohalogenation of the beta isomer, as evidenced by its extremely low rate of reaction in comparison with the other isomers, appears to justify the concept of the "beta ring" of chlorines, in which, it is

presumed, there would be a high degree of steric hindrance. The order of reactivities of the other isomers, $\alpha, \delta > \gamma \gg \beta$, coincides with the proposed structures arising from the statistical treatment of the

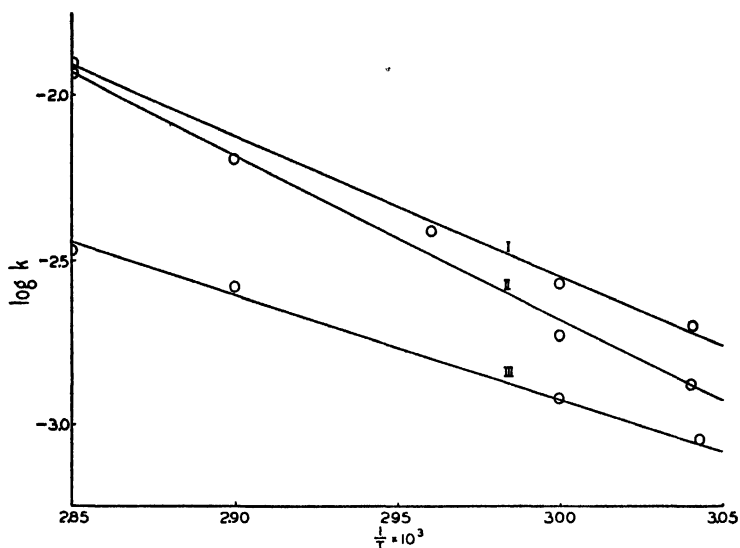


FIG. 5. Relation of $\log k$ to $\frac{1}{T}$ for the α , γ , and δ isomers. I, α ; II, δ ; III, γ .

TABLE II
ACTIVATION ENERGIES AND PZ VALUES FOR THE ISOMERS

Isomer	E , kilocalories	PZ
Alpha	19.5	2×10^{10}
Gamma	13.8	1×10^6
Delta	20.4	6×10^{10}

likelihood of formation of each isomer (1). These studies, although they are probably not conclusive, led to the assumption that the gamma isomer has one chlorine out of the beta ring, and the alpha and delta isomers each two. It is interesting to note that the active gamma isomer shows an intermediate reactivity, which indicates that the process of insecticidal action probably does not involve dehydrohalogenation. The proposed structure of the gamma isomer is sterically identical with the proven structure of the metabolite mesoinositol. The latter compound, hexahydroxycyclohexane, has several known geometrical isomers, all relatively unimportant physiologically. Attempts made in this laboratory to interconvert the active isomers of hexachlorocyclohexane and inositol, by hydrolysis or chlorination, have been unsuccessful.

Subsequent to the undertaking of this work, studies on the rate of dehydrochlorination of the hexachlorocyclohexane isomers were reported by Cristol (2) and by Kauer *et al.* (6), the latter including the epsilon isomer in the investigation. These workers used alcoholic sodium hydroxide rather than piperidine as the dehydrochlorination agent, but the experimental results are essentially in agreement. The epsilon isomer was reported to be somewhat less reactive than the gamma isomer.

Acknowledgment

Acknowledgment is made to the Defence Research Board for awarding a grant in aid of research on this project.

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SYNTHÈSES D'ACIDES AMINÉS PAR L'INTERMÉDIAIRE DES HYDANTOÏNES. DL-SÉRINE ET DL-CYSTINE¹

PAR GUY NADEAU ET ROGER GAUDRY

Résumé

Le méthoxyacétal obtenu du bromacétal avec un rendement de 78% fut transformé en aldéhyde, puis en cyanhydrine correspondante. La cyanhydrine, chauffée avec un excès de carbonate d'ammonium suivant la modification de Bucherer de la méthode de Strecker, donna la 5-méthoxyméthylhydantoïne avec un rendement de 52%. L'hydrolyse de l'hydantoïne avec de l'hydroxyde de baryum à 160° C. sous pression donna l'acide α -amino- β -méthoxypropionique qui fut hydrolysé en DL-sérine par la méthode usuelle. La réaction de Bucherer appliquée à l'éthoxyacétal, au chloracétal, au bromacétal, au méthylthioacétal et au benzylthioacétal donna la 5-éthoxyméthylhydantoïne, la 5-chlorométhylhydantoïne, la 5-bromométhylhydantoïne, la 5-méthylthiométhylhydantoïne et la 5-benzylthiométhylhydantoïne avec des rendements respectifs de 36%, 63%, 29%, 28% et 76%. L'hydrolyse de la 5-méthylthiométhylhydantoïne et de la 5-benzylthiométhylhydantoïne au moyen de l'hydroxyde de baryum à 160° C. sous pression donna la S-méthylcystéine et la S-benzylcystéine avec des rendements respectifs de 75% et 68%. L'hydrolyse de la 5-chlorométhylhydantoïne avec de l'acide chlorhydrique à 20% sous pression à 130° C. donna 56% d'acide α -amino- β -chloropropionique que l'hydroxyde d'argent permet de transformer en DL-sérine.

Introduction

La première synthèse de la DL-sérine par la méthode de Strecker (16) a été faite par Fischer et Leuchs (8) à partir de l'aldéhyde glycolique. A cause de l'instabilité relative de ce produit de départ, Leuchs et Geiger (12) lui substituèrent l'éthoxyacétaldéhyde qu'ils obtinrent du chloracétal. Plus récemment Dunn *et al.* (5) préparèrent l'éthoxyacétaldéhyde par oxydation de l'éther monoéthylique du glycol d'éthylène, produit commercial facilement accessible, et décrivirent la première méthode pratique de synthèse de la sérine par la méthode de Strecker. Mais la sérine n'avait jamais encore été préparée en passant par les hydantoïnes substituées en position 5 d'après la modification de Bucherer (3) de la méthode classique de Strecker.

Nous avons préparé la 5-méthoxyméthylhydantoïne ainsi que la 5-éthoxyméthylhydantoïne à partir du chloracétal et du bromacétal par l'intermédiaire du méthoxyacétal et de l'éthoxyacétal. Leuchs et Geiger (12) avaient eux-mêmes utilisé le chloracétal dans la préparation de l'éthoxyacétal d'après la méthode décrite par Lieben (14) tandis que Pinner (15) et Levene et Schormuller (13) lui avaient substitué le bromacétal. Nous avons étudié la possibilité de remplacer l'éthoxyacétal par le méthoxyacétal. En simplifiant la méthode de Leuchs et Geiger, nous avons obtenu le méthoxyacétal avec un rendement de 71% et l'éthoxyacétal avec un rendement de 63% à partir

¹ Manuscrit reçu le 16 octobre 1948.

Contribution du Département de biochimie de la Faculté de médecine, Université Laval, Québec, Canada. Extrait de la thèse présentée par Guy Nadeau à l'École des gradués de l'Université Laval pour l'obtention du grade de docteur ès sciences physiques.

du chloracétal. Toutefois le fractionnement du méthoxyacétal ou de l'éthoxyacétal en présence de chloracétal non transformé est difficile et, comme l'avaient d'ailleurs indiqué Leuchs et Geiger, il est pratiquement impossible d'éviter la présence de chlore dans les produits des réactions subséquentes.

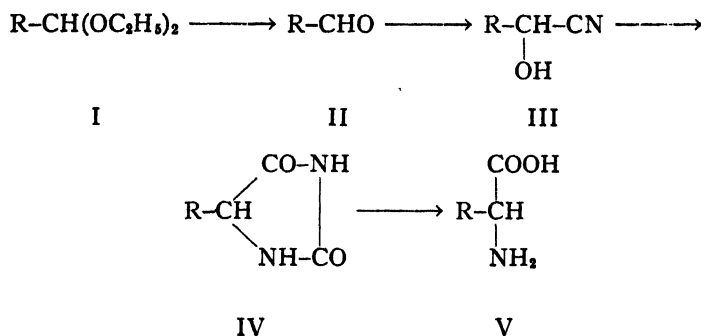
Afin de parer à cet inconvénient, nous avons alors substitué au chloracétal le bromacétal que nous avons préparé à partir de l'acétate de vinyle suivant la méthode de Bedoukian (2), mais avec un rendement de 87.5%. Nous avons ainsi porté le rendement en méthoxyacétal à 78% et en éthoxyacétal à 73.5%. Cette modification a en outre l'avantage de donner des produits exempts de brome à cause de la facilité de séparer par fractionnement le bromacétal non transformé.

Pour hydrolyser l'acétal (I) en aldéhyde correspondante (II) (6, 11, 12), nous avons trouvé que les meilleures conditions consistaient à traiter l'acétal par un acide minéral 5 *N* et à agiter le tout efficacement à la température de la chambre. Sans qu'il soit nécessaire d'isoler l'aldéhyde de sa solution aqueuse, nous en avons préparé le dérivé bisulfite, puis la cyanhydrine (III) qui fut extraite à l'éther de la solution aqueuse. Le chauffage de la cyanhydrine avec un excès de carbonate d'ammonium (3) a donné la 5-méthoxyméthylhydantoïne avec un rendement de 52% à partir du méthoxyacétal et la 5-éthoxyméthylhydantoïne avec un rendement de 36% à partir de l'éthoxyacétal. Il est à noter toutefois que la 5-méthoxyméthylhydantoïne est beaucoup plus facile à isoler à l'état pur et à recristalliser que le composé éthoxylé et, comme le méthoxyacétal s'obtient lui-même avec un meilleur rendement, il n'y a donc pas d'avantage à effectuer cette synthèse de la sérine par l'intermédiaire du dérivé éthoxylé.

Nous avons hydrolysé la 5-méthoxyméthylhydantoïne au moyen de l'hydroxyde de baryum en acide α -amino- β -méthoxypropionique, composé difficilement cristallisable, mais que nous avons identifié sous forme d'acide α (β -phényluréido)- β -méthoxypropionique. L'hydrolyse de cet acide aminé suivant la méthode décrite par Carter et West (4, p. 82) a donné la DL-sérine avec un rendement de 72.4% à partir de la 5-méthoxyméthylhydantoïne, soit un rendement de 37.7% à partir du méthoxyacétal.

Nous avons aussi appliqué au chloracétal et au bromacétal la réaction de Bucherer (3) et nous avons obtenu la 5-chlorométhylhydantoïne et la 5-bromométhylhydantoïne avec des rendements respectifs de 63% et 29%. L'instabilité plus grande de l'hydantoïne bromée en milieu alcalin explique le faible rendement obtenu comparativement à l'hydantoïne chlorée. Pour la même raison, nous avons effectué l'hydrolyse de la 5-chlorométhylhydantoïne en acide DL- α -amino- β -chloropropionique au moyen de l'acide chlorhydrique à 20% sous pression, avec un rendement de 56%. A notre connaissance, la synthèse directe de cet acide aminé n'avait pas été réalisée auparavant, mais il avait été préparé à partir de la sérine par Fischer et Raske (9) et Erlenmeyer et Stoop (7) comme intermédiaire au cours de leur synthèse de la cystine.

Nous avons ensuite transformé l'acide DL- α -amino- β -chloropropionique en DL-sérine au moyen de l'hydroxyde d'argent avec un rendement de 87%, soit 31% à partir du chloracétal.



R = méthoxyméthyl, ($\text{CH}_3\text{-O-CH}_2\text{-}$); éthoxyméthyl, ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-}$); chlorométhyl, ($\text{Cl-CH}_2\text{-}$); bromométhyl, ($\text{Br-CH}_2\text{-}$); méthylthiométhyl, ($\text{CH}_3\text{-S-CH}_2\text{-}$); benzylthiométhyl, ($\text{C}_6\text{H}_5\text{-CH}_2\text{-S-CH}_2\text{-}$).

Le passage de la 5-chlorométhylhydantoïne ou de la 5-bromométhylhydantoïne à la 5-méthoxy- ou à la 5-éthoxyméthylhydantoïne s'est avéré impossible à cause de l'insolubilité de ces hydantoïnes halogénées dans l'alcool absolu. Toutefois nous avons préparé l'hydantoïne correspondante de la sérine, la 5-hydroxyméthylhydantoïne, à partir de la 5-chlorométhylhydantoïne au moyen de l'hydroxyde d'argent.

Nous avons en outre préparé la 5-méthylthiométhylhydantoïne et la 5-benzylthiométhylhydantoïne avec des rendements respectifs de 28.4% et 76.5% à partir du méthylthioacétal et du benzylthioacétal. Ces acétals avaient déjà été préparés respectivement par Barger et Coyne (1) et Hutchison et Smiles (10). Toutefois, en simplifiant leurs méthodes et en substituant le bromacétal au chloracétal, nous avons porté les rendements en méthylthioacétal et en benzylthioacétal à 88.5% et 80% respectivement. L'hydrolyse des hydantoïnes avec de l'hydroxyde de baryum à 160° C. sous pression nous a donné la S-méthylcystéine et la S-benzylcystéine avec des rendements de 75% et 68%.

A notre connaissance, la synthèse directe de la S-méthylcystéine n'avait pas été décrite antérieurement. Cet acide aminé avait été préparé par méthylation de la DL-cystéine par duVigneaud, Loring et Craft (17). La S-benzylcystéine avait été préparée par Wood et duVigneaud (18), à partir du sulfure de chlorométhylbenzyle par condensation avec le phthalimidomalonate d'éthyle et hydrolyse, comme intermédiaire dans leur synthèse de la DL-cystine.

Le rendement total en DL-cystine à partir du bromacétal est donc de 33% puisque l'hydrolyse de la S-benzylcystéine au moyen du sodium dans l'ammoniac liquide se fait avec un rendement de 80%.

Partie expérimentale

Alkoxyacétals (I)

Un mélange de bromacétal (0.2 mole) et d'une solution de méthylate ou d'éthylate de soude (0.2 mole de sodium dans 100 ml. de méthanol ou d'éthanol absolus) fut chauffé dans un autoclave à 105°-110° C. pendant une heure, puis refroidi et versé dans 500 ml. d'eau froide. L'acétal fut extrait à l'éther et la solution étherée fut séchée sur du sulfate de soude. Après distillation de l'éther, l'acétal fut distillé dans le vide. Le tableau I décrit les propriétés et les rendements de ces acétals.

TABLEAU I

ACÉTALS

Acétal	Produit de départ	Rendement, %	P.é., ° C.
Méthoxyacétal	Chloracétal	71	48-50 (19 mm.)
"	Bromacétal	78	
Éthoxyacétal	Chloracétal	63	71-72 (25 mm.)*
"	Bromacétal	73.5	
Méthylthioacétal	Bromacétal	88.5	91 (25 mm.)†
Benzylthioacétal	Bromacétal	80	178 (25 mm.)‡

* 72° à 74° C. (26 mm.) (12).

† 188° à 190° C. (760 mm.) (1).

‡ 192° à 195° C. (30 mm.) (10).

Thioacétals (I)

A une solution d'éthylate de soude (0.2 mole de sodium dans 200 ml. d'éthanol absolu), refroidie dans un bain de glace et de sel, furent ajoutées lentement le méthyl ou le benzyl mercaptan (0.2 mole) liquide, préalablement refroidi, puis le bromacétal (0.2 mole). Le mélange fut chauffé à reflux pendant deux heures, refroidi et versé dans 500 ml. d'eau froide. L'acétal fut extrait à l'éther et la solution étherée fut séchée sur du sulfate de soude. Après distillation de l'éther, l'acétal fut distillé dans le vide. Le tableau I décrit les propriétés et les rendements de ces acétals.

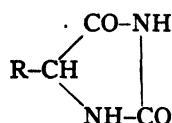
Hydantoïnes (IV)

Un mélange de l'acétal (0.1 mole) et de 20 ml. d'acide chlorhydrique 5 N fut agité à la température de la chambre pendant 24 h. A la solution refroidie et agitée furent ajoutées successivement du sulfite neutre de soude (0.1 mole), du sulfite acide de soude (0.1 mole) et une solution de cyanure de potassium (0.1 mole) dans 50 ml. d'eau. Le mélange fut agité pendant deux heures à la température de la chambre. Après extraction à l'éther et distillation de l'éther dans un vide partiel, la cyanhydrine résultante fut ajoutée à un mélange de carbonate d'ammonium (0.2 mole) et de 100 ml. d'alcool à 50%. Le mélange fut agité pendant deux heures dans un bain-marie maintenu à 55° C. et l'excès de carbonate d'ammonium fut décomposé par distillation

dans le vide. La solution fut décolorée au noir animal, concentrée à petit volume et additionnée de deux ou trois volumes d'alcool bouillant. L'hydantoïne cristallise lentement à la glacière. Le tableau II décrit les propriétés et les rendements des hydantoïnes.

TABLEAU II

HYDANTOÏNES



R-	Rendement, %	P.f., ° C.	Formule	Analyse, %			
				Azote		Soufre ou halogène	
				Calculé	Trouvé	Calculé	Trouvé
5-méthoxyméthyl-	52.1	167-170 (sub.)*	C ₈ H ₉ O ₃ N ₂	19.44	19.37	—	—
5-éthoxyméthyl-	36.1	77	C ₉ H ₁₁ O ₃ N ₂	17.72	17.48	—	—
5-chlorométhyl-	63.2	170 (déc.)	C ₆ H ₈ O ₂ N ₂ Cl	18.85	18.99	23.88	23.90
5-bromométhyl-	28.7	165 (sub.)	C ₆ H ₈ O ₂ N ₂ Br	14.51	14.28	41.45	40.82
5-méthylthiométhyl-	28.4	154-155	C ₅ H ₈ O ₂ N ₂ S	17.50	17.50	20.00	18.85
5-benzylthiométhyl-	76.5	103-106	C ₁₁ H ₁₂ O ₂ N ₂ S	10.86	10.92	13.56	13.08

* Les points de fusion ne sont pas corrigés.

La cristallisation de la 5-chlorométhylhydantoïne se fait par évaporation de la solution aqueuse. Dans ce cas, l'addition d'alcool donne un précipité amorphe, non recristallisable. D'autre part, la 5-benzylthiométhylhydantoïne cristallise instantanément par agitation du résidu sec avec de l'éther de pétrole.

DL-Sérine

Un mélange de 7.2 g. de 5-méthoxyméthylhydantoïne, de 25.2 g. d'hydroxyde de baryum octahydraté et de 150 ml. d'eau fut chauffé dans un autoclave à 160° C. pendant 30 min. Le mélange fut refroidi et le carbonate de baryum formé fut filtré. Le filtrat fut agité avec 4.5 g. de carbonate d'ammonium et filtré de nouveau. L'excès de carbonate d'ammonium fut décomposé par distillation dans le vide et la solution fut évaporée à siccité. Le résidu brut de l'O-méthylsérine fut chauffé à reflux avec 40 ml. d'acide bromhydrique à 48% pendant deux heures et demie. La DL-sérine fut isolée suivant la méthode décrite par Carter et West (4). P.f. 240° C. (d.). Rendement: 3.8 g., 72.4%. Calculé pour C₃H₇O₃N: N, 13.33%. Trouvé: 13.28%.

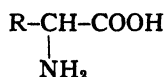
Acide α-Amino-β-chloropropionique

Un mélange de 3.0 g. de 5-chlorométhylhydantoïne et de 40 ml. d'acide chlorhydrique à 20% dans un tube scellé à vide fut chauffé pendant 36 h. à

125°-130° C. La solution fut évaporée à siccité et le chlorhydrate de l'acide aminé fut séparé du chlorure d'ammonium par dissolution dans l'alcool absolu bouillant. La solution fut additionnée d'un léger excès de pyridine et mise à la glacière. L'acide aminé brut fut recueilli par filtration, dissous dans l'eau, décoloré au noir animal et recristallisé par addition de deux volumes d'alcool bouillant. Le tableau III décrit les propriétés et le rendement de l'acide aminé.

TABLEAU III

ACIDES AMINES OBTENUS À PARTIR DES HYDANTOÏNES CORRESPONDANTES



Acide aminé	Rendement, %	P.f., ° C.	Formule	Analyse, %			
				Azote		Soufre ou halogène	
				Calculé	Trouvé	Calculé	Trouvé
O-méthylsérine*	80	—	—	—	—	—	—
Acide α-amino-β-chloropropionique	56	159-160(sub.)†	C ₂ H ₄ O ₂ NCI	11.33	11.20	28.74	28.43
S-méthylcystéine	75	240 (déc.)‡	C ₄ H ₉ O ₂ NS	10.37	10.22	23.70	22.88
S-benzylcystéine	68	215§	C ₁₀ H ₁₃ O ₂ NS	6.63	6.65	15.16	13.08

* Dérivé: acide α (β-phényluréido)-β-méthoxypropionique. P.f. 164° à 166° C. Calculé pour C₁₁H₁₄O₄N₂: N, 11.76%. Trouvé: N, 11.53%.

† Vers 160° C. (9).

‡ 248° C. (déc.) (17)

§ 215° à 216° C. (18).

DL-Sérine

Une solution de 2.0 g. d'acide α-amino-β-chloropropionique dans 50 ml. d'eau fut agitée pendant une heure à la température de la chambre avec 2 g. d'hydroxyde d'argent fraîchement préparé. Le mélange fut filtré et le filtrat fut débarrassé des sels d'argent par l'hydrogène sulfuré. Après filtration, la solution fut évaporée à siccité et le résidu fut dissous dans 10 ml. d'eau. A la solution refroidie à 0° C. et fortement agitée furent ajoutés 10 ml. d'éthanol absolu. L'agitation fut poursuivie pendant une heure à 0° C. puis le mélange fut mis à la glacière. La DL-sérine cristallise lentement. Rendement: 1.45 g., 86.8%. P.f. 240° C. (d.). Calculé pour C₃H₇O₂N: N, 13.33%. Trouvé: N, 13.20%.

5-Hydroxyméthylhydantoïne

Un mélange de 7.4 g. de 5-chlorométhylhydantoïne en solution dans 200 ml. d'eau et de 6.5 g. d'hydroxyde d'argent fraîchement préparé fut agité à la température de la chambre pendant 30 min. Le précipité formé fut séparé par centrifugation et les dernières traces de sel d'argent furent précipitées

par l'hydrogène sulfuré. La solution résultante fut décolorée au noir animal et évaporée à siccité. Le résidu fut cristallisé par agitation avec 50 ml. d'alcool absolu. P.f. 140° C.(sublime). Calculé pour $C_4H_6O_3N_2$: N, 21.54%. Trouvé: N, 21.49%.

S-méthyl- et S-benzylcystéine

Un mélange de l'hydantoïne (0.05 mole); de 25.2 g. d'hydroxyde de baryum octahydraté et de 150 ml. d'eau fut chauffé dans un autoclave à 160° C. pendant 30 min. Le mélange fut agité avec 4.5 g. de carbonate d'ammonium et la carbonate de baryum filtré. L'excès de carbonate d'ammonium fut décomposé par distillation dans le vide. La solution fut décolorée au noir animal, concentrée à petit volume, additionnée de trois volumes d'alcool bouillant et mise à la glacière. Le tableau III décrit les propriétés et les rendements des acides aminés.

Remerciements

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INFLUENCE OF THE AMINO ACID - DEXTROSE REACTION ON GROWTH OF LACTIC ACID BACTERIA¹

BY DYSON ROSE AND RUTH PETERSON

Abstract

Growth of *Lactobacillus arabinosus*, *L. casei*, and *Streptococcus faecalis* (as measured by lactic acid production) was studied in relation to the effects of the products of the amino acid - reducing sugar (Maillard) reaction. Addition of preformed Maillard products to a medium had little or no effect. Medium that had been autoclaved after the addition of dextrose promoted more rapid growth (shorter lag phase) than medium for which the dextrose had been autoclaved separately. This effect could not be traced to the presence of Maillard products, but appeared to be a complex phenomenon depending in part on the *Eh* of the solution. Destruction of amino nitrogen occurred during autoclaving, and destruction of tryptophan was evident from a comparison of growth response curves. It is concluded that the Maillard reaction affects the growth of these organisms only when an essential amino acid (or other nutrient), present in limiting quantities, is destroyed by the reaction. A serious error may be introduced into microbiological assays for amino acids if the samples to be assayed contain dextrose.

Introduction

Dextrose-containing media for the culture of micro-organisms darken in color when autoclaved. The darkening is a function of time and temperature, and, when it is intense, growth of some organisms is frequently less vigorous. Recent studies have led to recognition of much of the darkening of media during heat sterilization as an example of the amino acid - reducing sugar (Maillard (4)) reaction. It appeared possible, therefore, that products formed by the reaction of amino acids with dextrose might have inhibitory effects on the growth of some species of bacteria, and the present work was undertaken to determine the extent to which this inhibition might affect species commonly used in microbiological assays.

Stanier (11) presented evidence to show that heat sterilization of glucose in the presence of mineral salts rendered it toxic to *Cytophaga*, but Fahraeus (1) was unable to confirm this finding even for the same species. Hill and Patton (3) showed that the growth response of *Streptococcus faecalis* to given tryptophan levels was lowered if dextrose was heat sterilized with the other constituents of the medium but concluded (7) that this was due to a destruction of tryptophan.

The studies with *Cytophaga* (1, 11) were conducted using a medium containing no protein or amino acid nitrogen, and which, therefore, could not have contained Maillard products. In studies requiring more complex media, two types of products may be present after heat sterilization (true carameliza-

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tion products and the nitrogen-containing products of the Maillard reaction) and it would be desirable to distinguish between them but, to our knowledge, no method is available.

Materials and Methods

Three organisms commonly used for vitamin and amino acid assays were chosen: *Lactobacillus arabinosus* (8014),* *L. casei* (7569),* and *S. faecalis* (9790).* Transfers from stab cultures to a complete liquid medium were made 24 hr. before test solutions were to be inoculated. Inoculum was prepared by centrifuging the organisms from the liquid medium, resuspending them in 2 ml. of 1% saline, and diluting four drops of this suspension with approximately 20 ml. of saline. One drop of dilute suspension was used to inoculate 10 ml. of culture medium.

Two types of media were used in the studies: the synthetic medium used for amino acid assays (similar to that of Stokes *et al.* (12)), and the casein hydrolyzate medium used for niacin or tryptophan assay (similar to that of Greene and Black (2) and Snell and Wright (10)). In some tests, dextrose was added before autoclaving so that Maillard product was formed *in situ*, in others the medium was prepared in the normal manner except that no dextrose was added; then 5 ml. of a 2% solution of dextrose, containing Maillard product if desired, was added to each tube of medium after autoclaving (total volume, 10 ml.). In a few experiments medium containing dextrose was sterilized by Seitz filtration.

Maillard product was formed for subsequent addition to a medium by subjecting a mixture of dextrose and casein hydrolyzate (General Biochemicals Ltd.) to a temperature of 140° F. for several days. In the absence of a suitable method for determining the type of reaction (caramelization or Maillard) that had occurred, all fluorescent compounds formed in the presence of amino acids were assumed to be Maillard products. The concentration of these compounds in the media was estimated by determining the relative fluorescence with a Coleman Model 12 photofluorometer and B₁ and PC₁ filters.

The extent of growth of the organisms was determined by titrating the 10 ml. of culture medium with 0.1 *N* sodium hydroxide and the results are presented as milliliters of sodium hydroxide used.

Results

Effect of Various Factors on Initial Growth of the Organisms

The rate of growth of these organisms was compared in medium prepared and autoclaved in the normal manner, medium to which sterile dextrose solution was added after autoclaving, and medium that had been sterilized by Seitz filtration.

* American Type Culture Collection Numbers.

The results are given in Figs. 1 and 2, and show that, in contrast to the normally autoclaved medium, little or no growth of *L. arabinosus* or of *L. casei* occurred during the first 24 hr. in medium for which the dextrose was

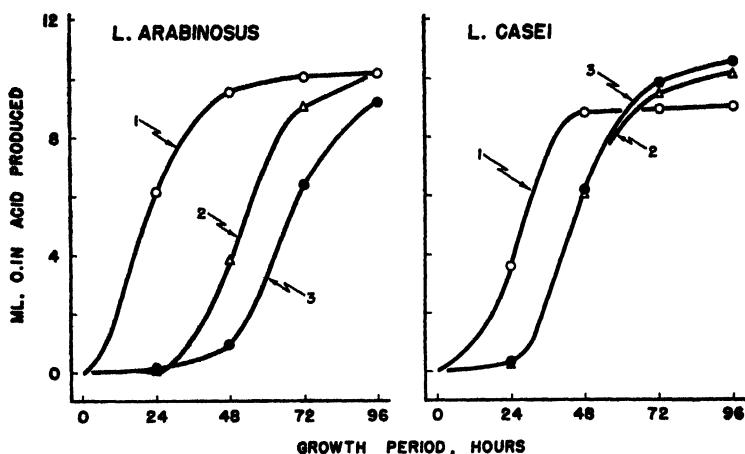


FIG. 1. Effect of autoclaving amino acid assay medium on acid production.

1. Medium autoclaved with dextrose, fluorescence 27.5.
2. Medium Seitz filtered, fluorescence 9.0.
3. Dextrose autoclaved separately, fluorescence 9.0.

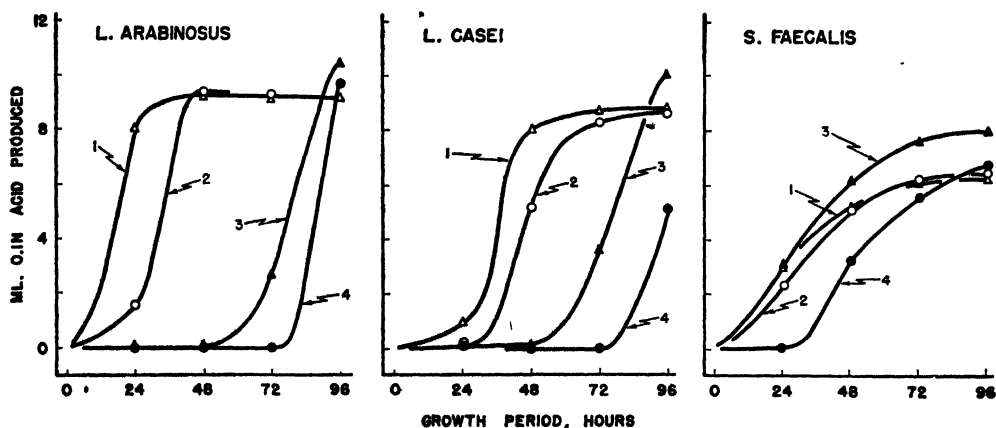


FIG. 2. Effect of the weight of inoculum on acid production in autoclaved and unautoclaved amino acid assay medium.

1. Medium autoclaved with dextrose, fluorescence 64, heavy inoculum.
2. Medium autoclaved with dextrose, fluorescence 64, light inoculum.
3. Dextrose autoclaved separately, fluorescence 9.0, heavy inoculum.
4. Dextrose autoclaved separately, fluorescence 9.0, light inoculum.

autoclaved separately. In a medium sterilized by Seitz filtration, a similar but less pronounced extension of the lag or induction period was observed. This prolongation of the lag phase was most marked if a light inoculum was used but was evident even in normally inoculated cultures (Fig. 2). *S. faecalis* was much less sensitive to factors inducing the prolonged lag phase than

were the two species of *Lactobacilli*; nevertheless, when a light *S. faecalis* inoculum was used, a slight but distinct prolongation of the lag phase occurred.

Attempts were made to duplicate this stimulatory effect of autoclaving by adding preformed Maillard products. Control tubes were autoclaved after the addition of dextrose; the others received, after autoclaving, a separately sterilized solution of dextrose that contained widely varying amounts of Maillard product. The results were not entirely consistent but indicated that initial growth was not influenced by the mere presence of Maillard product but depended upon some secondary factor introduced when the reaction occurred in the medium.

Results obtained when the initial pH of the medium was carefully controlled are presented in Fig. 3. These data show that the effect of autoclaving on the pH was not a critical factor.

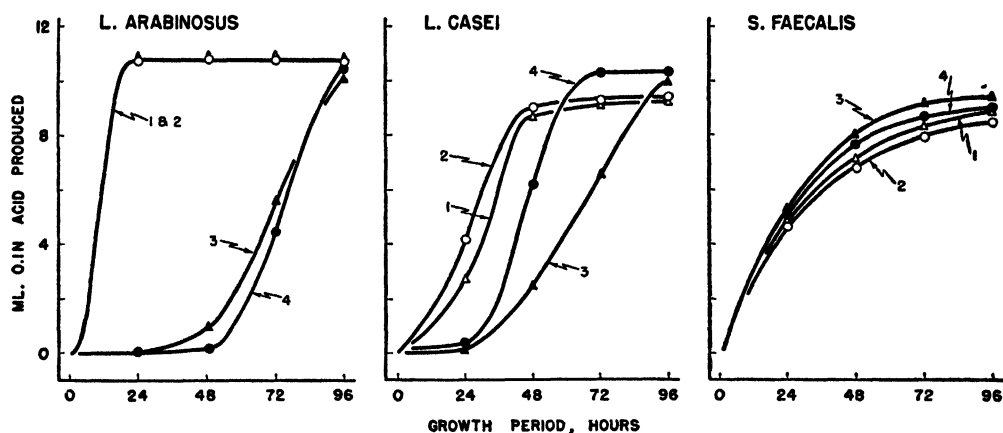


FIG. 3. Effect of autoclaving amino acid medium, and of pH, on acid production.

1. Medium autoclaved with dextrose, initial pH 6.78, final pH 6.51, fluorescence 26.
2. Medium autoclaved with dextrose, initial pH 6.51, final 6.32, fluorescence 22.
3. Dextrose autoclaved separately, initial pH 6.78, final 6.78, fluorescence 9.5.
4. Dextrose autoclaved separately, initial pH 6.51, final 6.52, fluorescence 9.5.

To change the oxidation-reduction potential of the medium a solution of ascorbic acid (20 mgm. in 250 ml.) and dextrose, sterilized by Seitz filtration, was added to one lot of medium before autoclaving. Growth in this lot, as shown in Fig. 4, greatly exceeded that in the tubes for which dextrose had been autoclaved separately and, with two organisms, exceeded that in normally autoclaved medium.

Determination of the *Eh* of these complex solutions gave results of doubtful significance. While the *Eh* of medium containing ascorbic acid was invariably negative (-0.03 to -0.04 v.), that of normal medium varied from $+0.02$ to $+0.08$ v. Medium autoclaved with dextrose tended to give lower values than that for which the dextrose had been autoclaved separately, but medium with added Maillard product sometimes gave still lower *Eh*

values. Within this range ($+0.02$ to $+0.08$ v.) no correlation between the early growth rate of the organisms (24 hr. titer) and the *Eh* could be found.

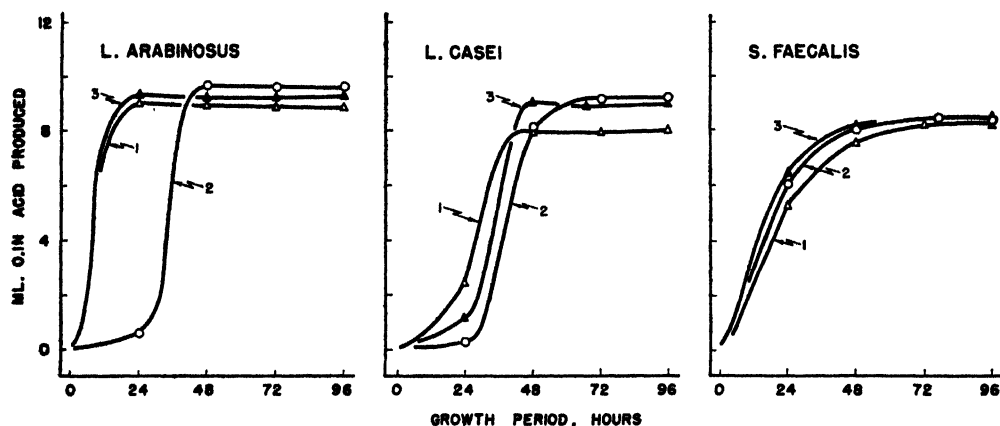


FIG. 4. Effect of autoclaving tryptophan assay medium, and of ascorbic acid, on acid production.

1. Medium autoclaved with dextrose, fluorescence 48.
2. Dextrose autoclaved separately, fluorescence 16.5.
3. Ascorbic acid added to medium, fluorescence 14.5.

Effect of Various Factors on Total Growth of the Organisms

When the dextrose is autoclaved with other constituents of the medium, reactions occur that destroy some dextrose. When Maillard products are formed externally to the medium a variable amount of dextrose usually remains unaffected by the reaction and is added to the medium with the Maillard products. This could be avoided by using the insoluble type of Maillard product but such material is not typical of that formed in media under the usual conditions of autoclaving. It was thus impossible to vary the amount of Maillard product in the medium without varying the sugar content but, in spite of this difficulty, attempts were made to determine the effect of Maillard product on total growth of the organisms.

For this purpose, varying amounts of a solution of Maillard products were added to weighed quantities of dextrose and the total volume made to 100 ml. After autoclaving, these solutions were dispensed to tubes of dextrose-free medium. For Expt. I of Table I the amount of dextrose was varied so that the total amount present, if none had been destroyed in the Maillard reaction, would have been 2 gm. per 100 ml. For Expts. II and III, 2 gm. of dextrose was used in each solution and the original dextrose content has been calculated to include that of the dextrose-casein hydrolyzate mixture.

The data presented in Table I show that total acid production by the two *Lactobacilli* paralleled the original dextrose content, and decreased with increasing fluorescence only in Expt. I in which no dextrose was added to offset that destroyed by the Maillard reaction. The total acid production by

TABLE I

EFFECT OF MAILLARD PRODUCT AND DEXTROSE CONCENTRATION
ON THE TOTAL ACID PRODUCTION

Ml. of Maillard solution	Original dextrose, %*	Fluorescence	Ml. of 0.1 N acid produced in 120 hr.		
			<i>L. arabinosus</i>	<i>L. casei</i>	<i>S. faecalis</i>
Expt. I					
0	2.00	7	9.64	10.72	—
2.5	2.00	165	9.75	9.40	—
5.0	2.00	300	8.60	8.20	—
7.5	2.00	415	7.66	7.28	—
10.0	2.00	500	6.43	6.11	—
Expt. II					
0	2.00	11	10.54	10.42	7.59
2.5	2.23	780	11.31	11.27	7.91
5.0	2.45	2250	12.02	12.03	7.98
7.5	2.63	3100	13.07	12.83	8.03
Expt. III					
0	2.00	10	10.44	10.09	8.65
1	2.09	310	10.68	10.30	8.35
2	2.18	560	11.19	10.67	8.31
3	2.27	800	11.26	10.97	8.00

* No. 1 of each experiment contained exactly the dextrose content shown; in the remainder, some dextrose had been destroyed in the formation of Maillard products.

S. faecalis was less influenced by the original dextrose content of the medium and there is some evidence (Expt. III) of a mild toxicity. Even for this species, however, the toxicity is obviously very slight.

To confirm the influence of the available dextrose on total acid production, solutions of dextrose were prepared so that 5 ml. would supply 100, 110, 120, or 130 mgm. per tube. Tubes receiving these amounts were autoclaved after the addition of the dextrose, and other tubes were given exactly 100 mgm. after autoclaving. The results are presented graphically in Fig. 5A and indicate that, with both *L. arabinosus* and *L. casei*, acid production from 100 mgm. of dextrose added after autoclaving was equal to that from approximately 107.5 mgm. added before autoclaving. Many of the compounds in the medium, including the Maillard products, interfere in chemical methods of dextrose determination, and the latter are therefore not sufficiently accurate to corroborate this figure.

Similar experiments using *S. faecalis* did not show a linear relation between total acid production and dextrose content. This is believed to have been due to the low buffering capacity of the medium used.

Loss of an Essential Amino Acid from Media During Autoclaving

Formation of Maillard product in a medium involves the destruction of both dextrose and an amino acid. If the amino acid destroyed is essential, and is present in limiting quantities, its loss will reduce the growth of the

organism. The adequacy of autoclaved media used in these experiments, and of a "complete" yeast extract medium, was demonstrated by determining the growth response to increasing concentrations of dextrose. Data for *L.*

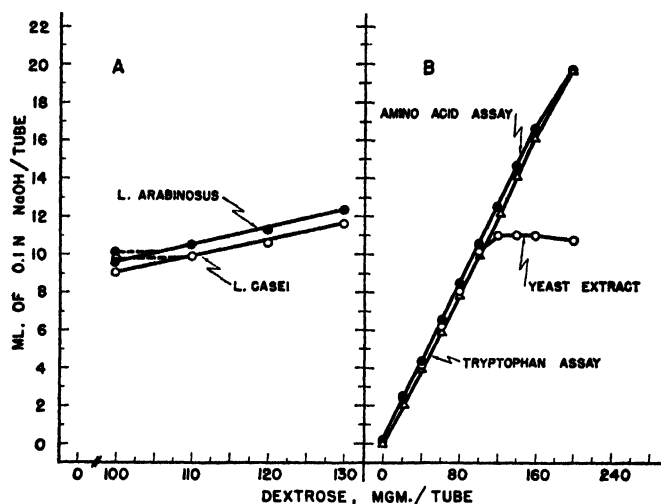


FIG. 5.

- A. Effect of dextrose concentration on the total acid production by *L. arabinosus* and *L. casei*.
- B. Effect of dextrose concentration on the total acid production by *L. arabinosus* in three types of media.

arabinosus are presented in Fig. 5B, and show that a direct linear response is obtained over a wide range of dextrose concentrations. With yeast extract medium some constituent other than dextrose obviously became limiting after the acid production reached 10.5 ml. *L. casei* behaved in a similar manner except that yeast extract medium was approximately equal to the others.

Total amino-nitrogen determinations, made by the micro Van Slyke manometric technique, showed that a considerable destruction of amino acids occurred during heat sterilization of tryptophan assay medium (Table II). Higher concentrations of dextrose led to a greater loss of amino nitrogen.

TABLE II
EFFECT OF AUTOCLAVING ON THE AMINO-NITROGEN
CONTENT OF MEDIA

Treatment	Dextrose content, %	Amino-nitrogen, mgm./10 ml.
Seitz filtered	2	3.93
Autoclaved	1	3.79
"	2	3.52
"	3	3.45

A loss of tryptophan was demonstrated by a lowered growth response. Typical curves obtained with *L. arabinosus* (standard microbiological procedures) are presented in Fig. 6A. Proof that the lowered growth response

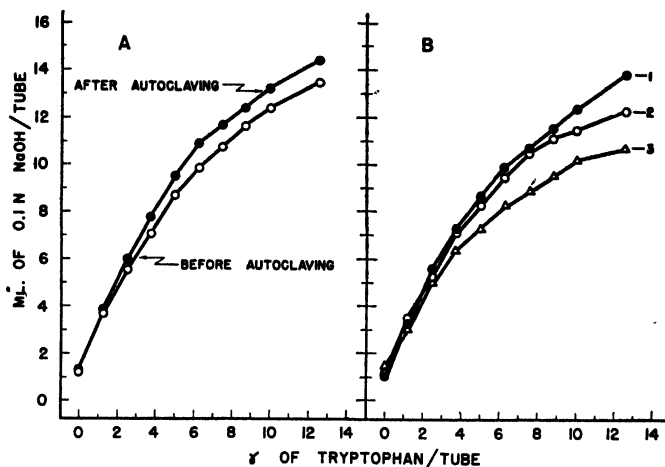


FIG. 6.

A. Effect of autoclaving on growth response to standard tryptophan levels.

B. Effect of dextrose on growth response to standard tryptophan levels.

1. 2% dextrose in medium, 0% in tryptophan standard.
2. 2% dextrose in medium, 10% in tryptophan standard.
3. 4% dextrose in medium, 10% in tryptophan standard.

was caused by destruction of tryptophan was obtained in a second experiment by adding, after autoclaving, amounts of tryptophan equivalent to the calculated amount destroyed. The resultant curve closely approximated that obtained when all of the tryptophan was added after autoclaving.

The effect of dextrose on the extent of the loss of tryptophan was tested by adding dextrose together with the tryptophan standard so that the amount of dextrose per tube increased progressively with increasing tryptophan. The results, presented graphically in Fig. 6B, show that the addition of dextrose along with the standard tryptophan significantly altered the growth response curve. This effect was more marked when the medium itself had a high dextrose content. It is thus apparent that a serious error may be introduced into microbiological assays for tryptophan if the sample to be assayed contains dextrose or presumably any other aldehyde, and that the error is greater in media of high initial dextrose levels.

Discussion and Conclusions

Orla-Jensen (6) appears to have been first to recognize the stimulatory effect of autoclaved media on *Lactobacilli*. As a possible explanation he suggested the formation of a complex growth factor. Smiley, Niven, and Sherman (9) observed this phenomenon with *S. salivarius*, and showed that

caramelized dextrose, pyruvic acid, or acetaldehyde, had a similar effect. Niven and Sherman (5) failed to observe any difference in the growth stimulating properties of autoclaved and unautoclaved media when studying *S. faecalis* or *S. zymogenes*, but Rabinowitz and Snell (8) observed poor growth of *S. faecalis* in unautoclaved medium, and found that the addition of a reducing agent, such as ascorbic acid or sodium thioglycollate, overcame the deficiency of the medium.

The results of the present work are essentially in agreement with those quoted. The diverse results previously obtained with *S. faecalis* are, at least in part, explained by the fact that improved growth in autoclaved media was apparent only when a light inoculum was used. In agreement with the results of Rabinowitz and Snell (8) ascorbic acid has been found to stimulate initial growth of the *Lactobacilli*, but it appears probable that this effect was not entirely due to its reducing properties. Maillard products have mild reducing properties, but when formed externally and added to the medium, they failed to stimulate the initial growth. Furthermore, Seitz filtered medium and medium for which the dextrose had been autoclaved separately appeared to possess the same *Ek*, but the former usually supported better initial growth than the latter. Probably some additional factor is involved.

Under the conditions used in our studies, the apparent inhibitions due to moderate concentrations of Maillard product do not appear to have been true inhibitions, but were the result of loss of available nutrient concomitant to the formation of Maillard product. This finding is in agreement with that of Rabinowitz and Snell (8), who showed that, under the conditions used by them, destruction of cystine and cysteine was responsible for the lowered growth. In the present work, destruction of both dextrose and tryptophan was responsible for lowered growth, and probably any essential amino acid, if initially present in limiting quantity, would behave similarly. Thus, there appears to be little direct evidence of toxic effects traceable to Maillard products, especially as regards lactic acid bacteria.

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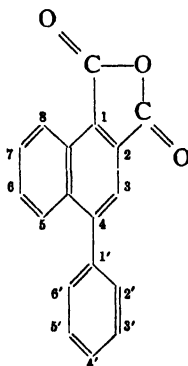
THE ULTRAVIOLET ABSORPTION SPECTRA OF SOME CARBOXY DERIVATIVES OF NAPHTHALENE¹

BY Y. HIRSHBERG AND R. NORMAN JONES

Abstract

The ultraviolet absorption spectra of a variety of naphthalene compounds containing phenyl and carboxy substituents are described. The majority of the compounds contain either the naphthalene-1,2-dicarboxylic acid anhydride or the naphthalene-2,3-dicarboxylic acid anhydride ring systems. It is shown that in ethanolic solution the spectra of these anhydrides change over a period of a few hours. The spectra of the anhydrides in *n*-heptane or dioxane solution do not change on standing. The effects of the various substituents are discussed in terms of steric inhibition of resonance and of antagonistic and reinforcing actions of the substituents, dependent on the position of substitution. The significance of these data are considered in relation to the general problem of the interpretation of the ultraviolet absorption spectra of complex molecules.

A systematic investigation of the reaction between 1,1-diarylethylenes and maleic anhydride, carried out at the Daniel Sieff Research Institute by Bergmann, Szmuszkovicz, and Fawaz (2, 3, 21), has made available a series of derivatives of 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (I) in which the substituents are alkyl, aryl, halogen, and methoxy groups.* Certain of these derivatives exhibited very intense fluorescence, and this observation prompted an investigation of their fluorescence and ultraviolet absorption spectra. These studies were extended subsequently to include simpler naphthalene compounds containing phenyl and carboxyl groups, and to related compounds in the naphthalene-2,3-dicarboxylic acid anhydride



I

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* Different systems of ring numbering are employed for these compounds in the publications cited in references (2) and (3). The system used in this paper corresponds with that adopted in the more recent publication (2) of Bergmann and Szmuszkovicz.

series. The ultraviolet absorption spectra are described below, and the fluorescence spectra will be dealt with in a subsequent publication.

I. EFFECTS OF CONJUGATED SUBSTITUENTS ON THE SPECTRUM OF NAPHTHALENE

The ultraviolet absorption spectrum of naphthalene consists of three parts which are designated A, B, and C in Fig. 1. The result of introducing a

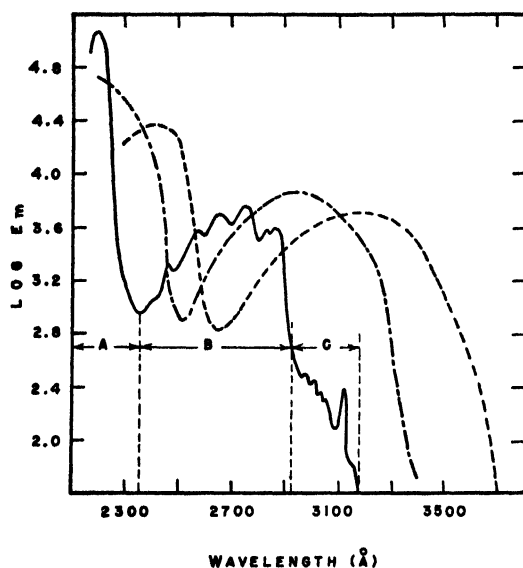


Fig. 1. 1-a ——— Naphthalene (ethanol)
1-b - - - - 1-Naphthylamine (ethanol)
1-c - · - · - 1-Naphthoic acid (ethanol)

conjugatable substituent at position 1 is shown in the spectra of 1-naphthylamine and 1-naphthoic acid in Curves 1-b and 1-c. The 1-substituent produces a large bathochromic displacement and broadening of band A. The B and C groups of bands become fused into a single band group, probably as a result of the broadening and bathochromic displacement of the B band group and its superposition on the weaker C band group.

The introduction of a conjugated substituent at position 2 produces changes of a different character (Curves 2-a, 2-b). The displacement of the A band is similar to that produced by the 1-substituent, but the B band group is hardly influenced by the introduction of the 2-substituent. The C band group is displaced bathochromically and greatly intensified. The indifference of the B band group to increased conjugation at position 2 parallels similar effects seen in other series of polynuclear aromatic hydrocarbons, such as the 4-substituted pyrenes, which have been described previously (9). Specific effects of conjugatable substituents on localized regions of the absorption spectrum have been discussed at length in connection with the spectrum of anthracene (10), and an attempt has been made to relate these to the direction of polarization of the associated processes of electronic excitation. In line with these

arguments, it may be suggested that the B band group in naphthalene is related to an excitation directed along the bb' -axis of the molecule (II), and that its displacement in the 1-substituted derivatives results primarily from the

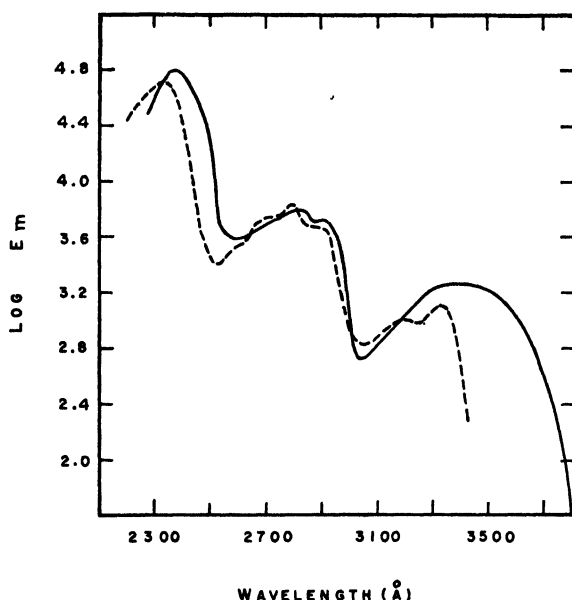
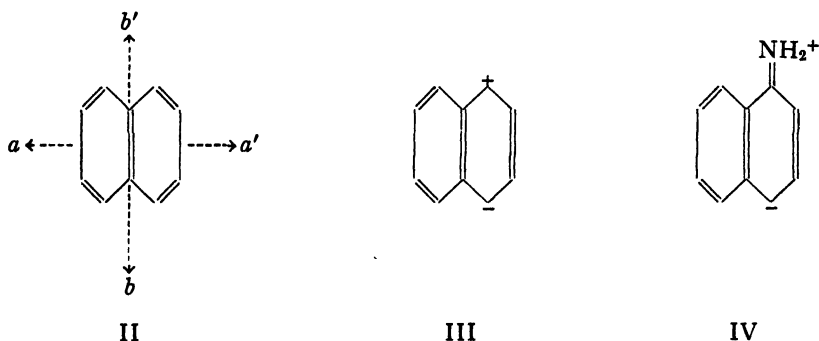


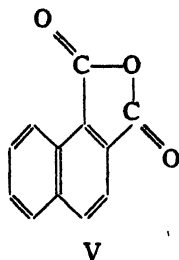
FIG. 2. 2-a ——— 2-Naphthylamine (ethanol)
2-b - - - - 2-Naphthoic acid (ethanol)

lowered energy of IV and related quinonoid structures in comparison with the corresponding structures (III) in the unsubstituted hydrocarbon.



Further insight into the effects of conjugation on the naphthalene spectrum is provided by naphthalene-1,2-dicarboxylic acid anhydride (V). In this compound conjugation at both positions 1 and 2 is operative, and the presence of the two carbonyl groups in the pentacyclic anhydride ring assures the whole conjugated system is planar so that the minimum S-effect and maximum C-effect is manifested.* The spectrum in *n*-heptane solution

* The symbols *C* (conjugation), *S* (steric), *Fs* (fine structure) and *B* (bathochromic) employed here to describe various categories of spectral shifts were introduced in an earlier paper (9) and described fully therein.



(Curve 3-a) shows a further bathochromic displacement of band A. The group of absorption bands appearing between 3100 and 3600 Å can possibly be divided into B and C groups as indicated.

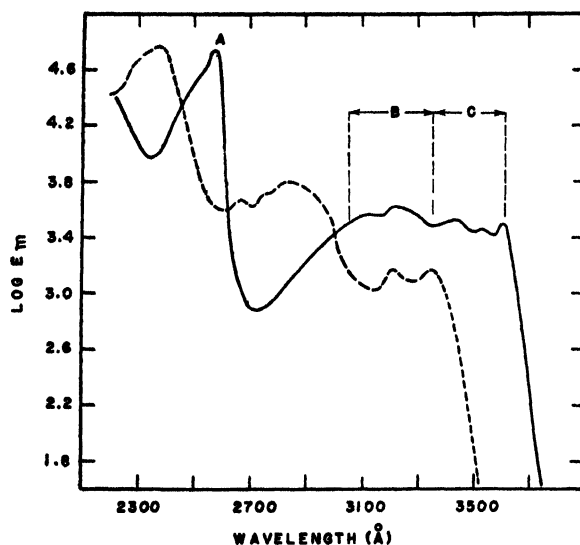


FIG. 3. 3-a ——— Naphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane) (V)
3-b - - - - Ditto (ethanol)

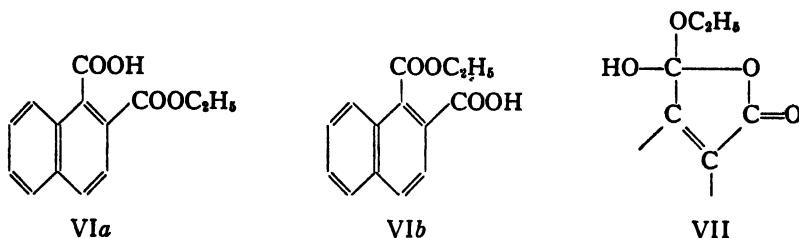
If this curve is compared with the spectrum of 1-naphthoic acid (1-c) an increase in the resolution of the fine structure at the longer wave lengths is the most prominent difference. This is in accord with previous observations (9) that such F_s effects are enhanced by cyclization.

The Reaction of Acid Anhydrides with Ethanol

When naphthalene-1,2-dicarboxylic acid anhydride is dissolved in ethanol, the spectrum undergoes a *slow* change, and, after a few hours a new stable spectrum is established (3-b). This phenomenon occurred invariably in all the derivatives of both the 1,2- and the 2,3-anhydrides examined.

Siegel and Moran (20) have reported that acid anhydrides react *instantaneously* with primary alcohols to form hemiesters. According to this hypothesis, the products formed on solution of naphthalene-1,2-dicarboxylic acid anhydride in ethanol would possess a structure VIa and VIb. Recently the reaction proposed by Siegel and Moran has been subject to criticism. Anderson

and Kenyon (1) could only isolate unchanged starting material after treating phthalic anhydride with ethanol for one hour at room temperature, while Lavine and Herkness (11) have questioned the interpretation of the titration data presented by Siegel and Moran in support of their hypothesis.



The changes in the ultraviolet absorption spectra observed in our experiments clearly demonstrate that under the conditions employed a chemical reaction does occur between the anhydride and ethanol. It involves a modification of the conjugated system, and a partial or complete esterification would appear to be the most logical reaction. An alternative might be addition of ethanol at one of the carbonyl groups to yield a product analogous to a hemiacetal (VII). Such products would be readily decomposed and this might account for the failure of Anderson and Kenyon to isolate any reaction product from phthalic anhydride and ethanol.

Wolf and Herold (26) have observed that aliphatic aldehydes react readily in dilute ethanol solution to form hemiacetals with complete disappearance of the carbonyl absorption band.

Further studies of the nature of these reaction products are being undertaken at Rehovoth; in the subsequent discussion in this paper the substances produced will be referred to merely as "ethanolysis products".

The spectrum of naphthalene-1,2-dicarboxylic acid anhydride is distinctly of the 1-substituted type, from which it may be argued that structures of type VIII in which the negative charge rests on the 1-carbonyl oxygen atom exert the dominant effect in determining the energy levels. On ethanolysis the spectrum changes to a 2-substituted type. In the ethanolysis product, therefore, the relative importance to the resonance of VIII and IX type structures is inverted.*

The spectrum of naphthalene-2,3-dicarboxylic acid anhydride (X) in *n*-heptane solution is shown in Curve 4-a. The structure of this compound provides for a maximal excitation of the 2-conjugated type of naphthalene substitution. In this spectrum the B band group is least influenced by the substituents, while the greatest effect is on the C band group, which is greatly

* If the ethanolysis product is a hemiester, the carboxyl or carboethoxy group at position 1 will be highly hindered by the large group at 2. This will force it out of the plane of the ring system and the hypsochromic displacement of the absorption must be attributed to the diminished conjugation between the 1-carbonyl group and the ring. The 2-carbonyl group, being hindered on one side only, will be less affected. If the ethanolysis results in addition of ethanol at one of the carbonyl groups (VII), it is the 1-carbonyl that would appear to be involved.

intensified and displaced bathochromically. These changes are similar in type, but greater in magnitude, than those that result from the introduction of the 2-carboxylic acid group.

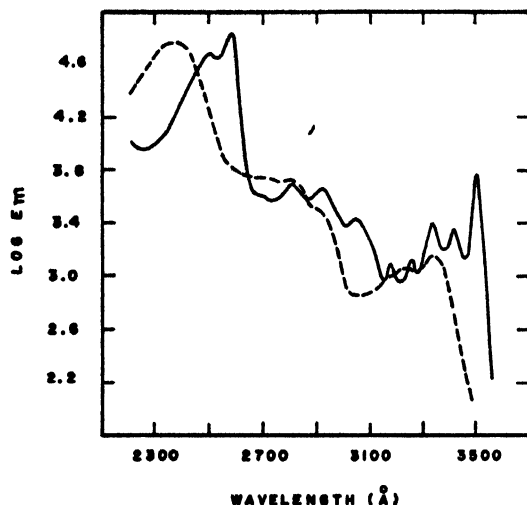
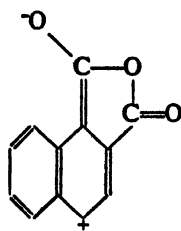
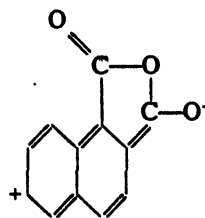


FIG. 4. 4-a ——— *Naphthalene-2,3-dicarboxylic acid anhydride (n-heptane) (X)*
4-b - - - - *Ditto (ethanol)*

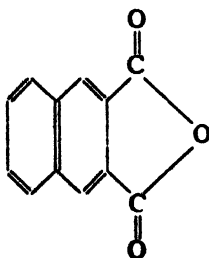


VIII



IX

In solution in ethanol the spectrum of naphthalene-2,3-dicarboxylic acid anhydride changes, and the stable spectrum that is finally established (Curve 4-b) closely resembles that of 2-naphthoic acid (Curve 2-b).



X

II. PHENYL DERIVATIVES OF NAPHTHALENE

The curves of 1-phenylnaphthalene (5-a) and 1-naphthoic acid (5-b) are similar, and may be contrasted with the spectrum of 1-naphthalacetone (XI)

(5-c) reproduced from the data of Wilds *et al.* (25). Friedel, Orchin, and Reggel, who have reported on the spectra of several aryl-naphthalenes (7), consider that in the 1-phenyl derivative the phenyl group is subject to strong

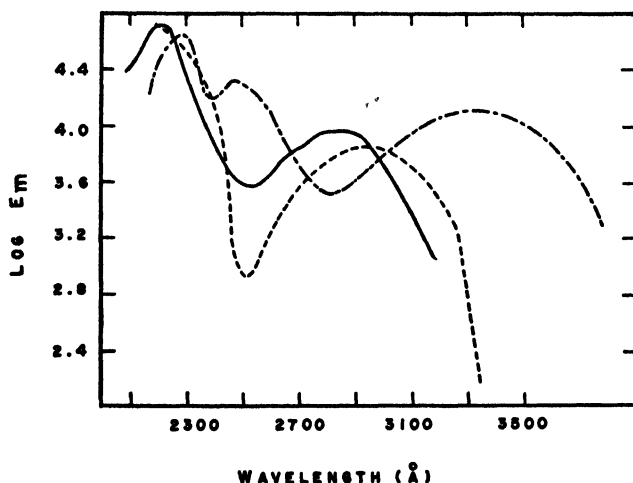
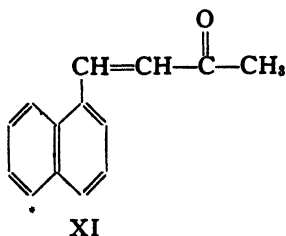


FIG. 5. 5-a ——— 1-Phenylnaphthalene (ethanol)
 5-b - - - - 1-Naphthoic acid (ethanol)
 5-c - · - · - 1-Naphthalacetone (ethanol) [XI]

steric hindrance, and that coupling between the benzene and naphthalene chromophores is sensibly diminished on this account. Comparison with the



spectrum of naphthalene and the other 1-substituted derivatives shown in Fig. 1 suggests that, although there is a significant S-effect in 1-phenylnaphthalene, it is by no means comparable with the strong steric effects noted in such compounds as 9,10-diphenylanthracene (10).

In Curves 6-a, 6-b, and 6-c the spectra of 2-phenylnaphthalene, 2-naphthoic acid, and 2-naphthalacetone are shown. The effects of steric factors on the spectrum of 2-phenylnaphthalene has been discussed previously (7, 8); in all these compounds unhindered planar structures may be postulated. Whereas the 2-carboxy and 2-phenyl groups leave the B band group of naphthalene relatively undisturbed, in the 2-naphthalacetone more complex changes occur.*

* In 2-phenylnaphthalene, structure analogous to the C absorption bands of 2-naphthylamine and 2-naphthoic acid is seemingly lacking. However, the measurements of the spectrum of 2-phenylnaphthalene have not been extended to log E_m values below 2.8.

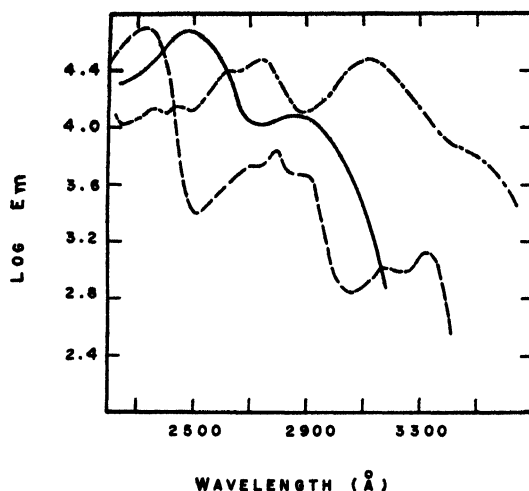


FIG. 6. 6-a ——— 2-Phenylnaphthalene (ethanol)
 6-b - - - - 2-Naphthoic acid (ethanol)
 6-c - · - · - 2-Naphthalacetone (ethanol)

III. 4-PHENYLNAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE

The spectrum of 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride is shown in Curve 7-a. Comparison with 7-b indicates that the introduction of

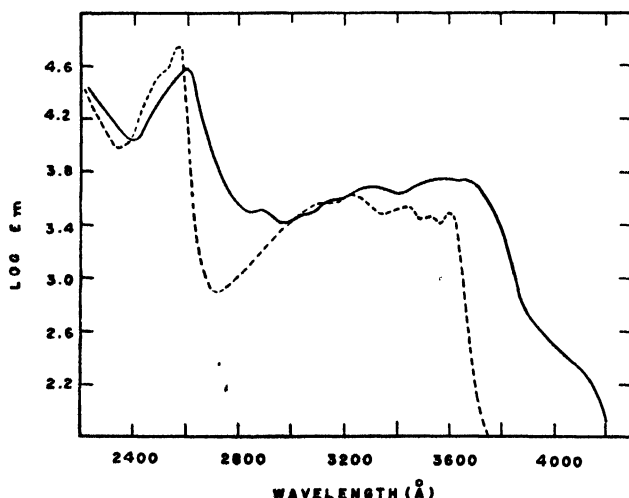


FIG. 7. 7-a ——— 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane) [I]
 7-b - - - - Naphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane) [V]

the 4-phenyl substituent causes significant changes. In the B and C band groups, the maxima are displaced bathochromically by 100 Å; the A band, however, is hardly affected. At long wave lengths the spectrum slopes off gradually and there is an indication of a new low intensity band extending into the visible.

In ethanolic solution the anhydride undergoes alcoholysis. The spectrum of the reaction product (8-a) closely resembles that of the monoester of V (8-b) save only for the band at 3900 Å. The similarity of 8-a and 8-b above 3500 Å

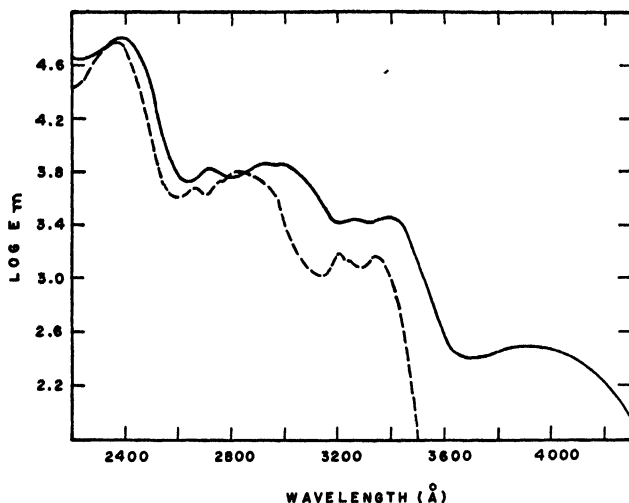


FIG. 8. 8-a ——— 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (ethanol)
8-b - - - - Naphthalene-1,2-dicarboxylic acid anhydride (ethanol)

is in accord with the observations made above that the conjugation in the molecule is diminished on reaction with ethanol.

The low intensity band at 3900 Å is difficult to account for. It was at first considered that it might arise from a trace of a strongly absorbing impurity, but this was discounted by the fact that similar bands are seen also in the spectra of a large number of derivatives of 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride prepared by independent syntheses. It is not influenced by the opening of the anhydride ring and its greater prominence in the spectra of the ethanolysis products results from the hypsochromic displacement of the remainder of the spectrum on ethanolysis.

IV. ALKYL, HALOGEN, AND METHOXYL DERIVATIVES OF 4-PHENYLNAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE

The introduction of a methyl group at the 4' position into 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride does not influence the general shape of the absorption curve; there is a small bathochromic displacement of the A and C groups of bands while the B band group is scarcely changed (Curve 9-a). This is true both of the spectra of the anhydride and of its ethanolysis product. The positions of the absorption maxima in the 4'-methyl, 4'-ethyl, 4'-isopropyl, 4'-tert. butyl derivatives are identical within the experimental limits of measurements (Table I). In this series of compounds there is no

indication of a hypsochromic shift in passing from the methyl to higher branched chain alkyl derivatives such as Matsen, Robertson, and Chuoke observed in a similar series of alkyl benzenes (13).

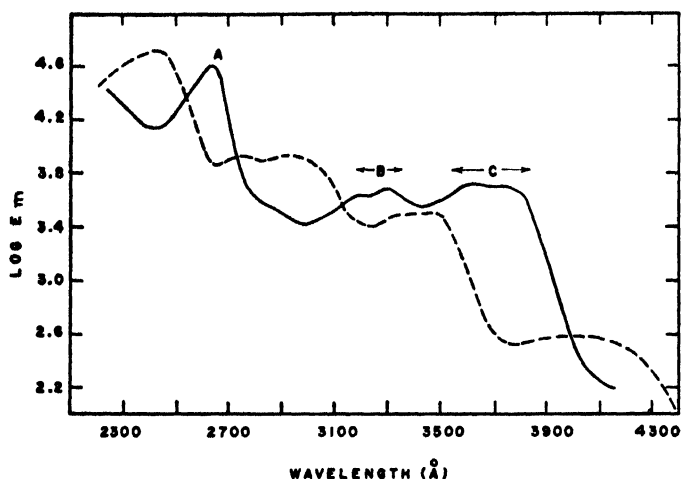
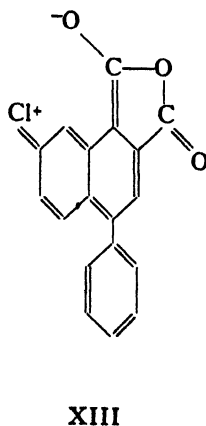
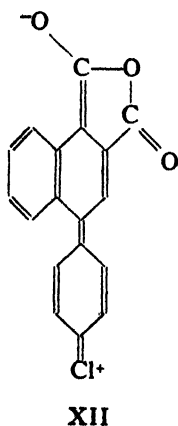


FIG. 9. 9-a ——— 4'-Methyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane)
9-b - - - - Ditto (ethanol)

Several halogen derivatives of 4-phenylnaphthalene-1,2-dicarboxylic anhydride have also been examined. These are listed in Table I, and contain fluorine, chlorine, and bromine substituents at positions 4' and 7. They also yield spectra that are almost identical with those of the 4'-methyl derivative. Although quinonoid structures like XII and XIII may be written for these compounds, their contributions to the resonance stabilization of the excited states must be comparable with that of the analogous structures in the corre-



sponding alkyl derivatives, where the positive charge is on a carbon atom of the ring. This is in agreement with observations on the spectra of halogen derivatives of other polynuclear aromatic hydrocarbons such as 2-chlorophenanthrene (9).

TABLE I
WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b	
			Wave length, Å	Intensity log <i>E</i> molar
Naphthalene	Ethanol	—	°	
1-Naphthylamine	Ethanol	—	2400 3220	4.36 3.71
2-Naphthylamine	Ethanol	—	^d	
1-Naphthoic Acid	Ethanol	i		
2-Naphthoic Acid	Ethanol	i		
Naphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	(2480)	4.54
			2560	4.74
			3080	3.59
			(3220)	3.56
			3440	3.54
			3540	3.45
			3600	3.50
	Ethanol		2680	3.67
			(2750)	3.71
			2820	3.83
			3200	3.19
			3340	3.18
	<i>n</i> -Heptane	iii	2500	4.58
			2570	4.78
			2810	3.69
			2930	3.67
			3040	3.44
			3180	3.10
			3260	3.15
			3340	3.45
			3420	3.36
			3500	3.81
	Ethanol		2360	4.77
			2710	3.72
			2800	3.74
			(2920)	3.48
			(3180)	3.02
			3220	3.06
			3340	3.12
1-Phenylnaphthalene	Ethanol	—		°

^a i. Eastman Kodak Company.

ii. Compound synthesized by F. Bergmann and J. Szmuszkovicz.

iii. Compound synthesized by E. Bergmann.

^b The more pronounced inflections are indicated by figures in parentheses.

^c See Friedel, Orchin, and Reggel (Ref. 7).

^d See Jones (Ref. 10).

^e The spectra in *n*-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

TABLE I—*Continued*WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA—*Continued*

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b	
			Wave length, Å	Intensity log <i>E</i> molar
1-Naphthalacetone	95% Ethanol	—		•
2-Phenylnaphthalene	Ethanol	—		†
2-Naphthalacetone	Ethanol	—		•
4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2600	4.61
			2880	3.52
			(3160)	3.58
			3300	3.70
			3570	3.75
			3660	3.73
	Ethanol		2380	4.77
			2720	3.81
			2910	3.86
			2990	3.86
			(3250)	3.45
			3400	3.48
			3880	2.50
	<i>n</i> -Heptane	ii	2645	4.64
			3200	3.64
			3300	3.70
			3620	3.72
			3750	3.70
	Ethanol		2450	4.72
			2750	3.92
			2910	3.94
			(3350)	3.50
			3450	3.50
			4000	2.61
4'-Ethyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2220	4.46
			2650	4.65
			3200	3.61
			3300	3.70
			3620	3.70
			3750	3.70
	Ethanol		2420	4.74
			2750	3.98
			3450	3.48
			4000	2.80

^a ii. Compound synthesized by F. Bergmann and J. Szmuszkovicz.^b The more pronounced inflections are indicated by figures in parentheses.

• See Wilds et al. (Ref. 25).

† See Jones (Ref. 8).

• The spectra in *n*-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

TABLE I—Continued

WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA—Continued

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b			
			Wave length, Å	Intensity log <i>E</i> molar		
4'-Isopropyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2220	4.44		
			2655	4.61		
			3200	3.71		
			3320	3.64		
			3620	3.65		
	3745		3.65			
	Ethanol		2460	4.79		
			2760	4.05		
			3440	3.56		
	4'-Tert. butyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride		<i>n</i> -Heptane	ii	2660	4.75
3210		3.69				
3325		3.77				
3620		3.81				
3745		3.74				
Ethanol		2460	4.84			
		2780	3.91			
		2940	3.99			
		3320	3.59			
		3450	3.69			
4000	2.34					
4',7-Dimethyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2645	4.65		
			3000	3.58		
			(3220)	3.71		
			3340	3.80		
			3660	3.81		
			3745	3.81		
			Ethanol	2440	4.75	
	2760			3.80		
	2960			3.92		
	(3360)			3.56		
	3450			3.60		
	4000			2.38		
	4'-Fluoro-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride			<i>n</i> -Heptane	ii	2600
			(2890)			3.46
(3190)		3.70				
3300		3.76				
3560		3.80				
3640		3.79				
Ethanol		2420	4.75			
		(2750)	3.72			
		2940	3.87			
		2990	3.88			
	3280	3.48				
3400	3.50					

^a ii. Compound synthesized by F. Bergmann and J. Szmuszkovicz.^b The more pronounced inflections are indicated by figures in parentheses.^c The spectra in *n*-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

TABLE I—*Continued*WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA—*Continued*

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b	
			Wave length, Å	Intensity log <i>E</i> molar
4'-Chloro-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	1,4-Dioxane	ii	2620	4.66
			(2900)	3.67
			3340	3.78
			3610	3.84
			3640	3.83
	Ethanol		2420	4.74
			2730	3.86
			3000	3.97
			3400	3.58
			(4000)	2.40
4'-Bromo-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2660	4.64
			(3170)	3.76
			3300	3.82
			3580	3.73
			3720	3.73
4'-Fluoro-7-methyl-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2645	4.64
			(3170)	3.68
			3310	3.68
			3630	3.69
			3750	3.69
	Ethanol		2450	4.62
			2750	3.89
			2900	3.89
			(3300)	3.46
			3450	3.46
4',7-Dichloro-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	4000	2.60
			2635	4.62
			(3170)	3.72
			3305	3.79
			3580	3.71
	Ethanol		3720	3.73
			2400	4.71
			2950	3.94
			3400	3.50
			4000	2.38
7-Methoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	<i>n</i> -Heptane	ii	2260	4.78
			2695	4.60
			(3180)	3.70
			3300	3.75
			3795	3.69
	Ethanol		3980	3.73
			2440	4.62
			2780	4.01
			(2900)	3.92
			(3440)	3.40
			3580	3.44
			4180	2.78

^a ii. Compound synthesized by F. Bergmann and J. Smuszkovics.^b The more pronounced inflections are indicated by figures in parentheses.^c The spectra in *n*-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

TABLE I—*Continued*WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA—*Continued*

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b			
			Wave length, Å	Intensity log <i>E</i> molar		
4',7-Dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	1,4-Dioxane	ii	2720	4.48		
			(3200)	3.64		
			3440	3.83		
			3880	3.83		
			4000	3.84		
	Ethanol		2430	4.67		
			3000	3.80		
			3370	3.53		
			3600	3.65		
			4260	2.52		
6,7-Dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride	n-Heptane	ii	2340	4.68		
			2750	4.57		
			3600	4.02		
	Ethanol		2580	4.74		
			3080	4.04		
			3920	2.60		
4,7-Diphenylnaphthalene-1-carboxylic acid	Ethanol	ii	2420	4.82		
			(2800)	4.50		
			3740	3.54		
1,6-Diphenylnaphthalene	Ethanol	ii	(2350)	4.50		
			2580	4.73		
			(3000)	4.00		
4,7-Diphenylnaphthalene-1,2-dicarboxylic acid anhydride	1,4-Dioxane	ii	2820	4.52		
			3440	3.77		
			3760	3.64		
	Ethanol		2460	4.74		
			2620	4.71		
			3400	3.35		
			(3550)	3.32		
			4,1'-Dinaphthyl-1,2-dicarboxylic acid anhydride	1,4-Dioxane	ii	2240
	2600					4.62
	(2730)					4.15
(2820)	4.00					
(2920)	3.87					
(3160)	3.62					
3320	3.70					
3620	3.76					
Ethanol	2240	4.81				
	2380	4.70				
	2820	4.07				
	(3250)	3.55				
	3380	3.55				

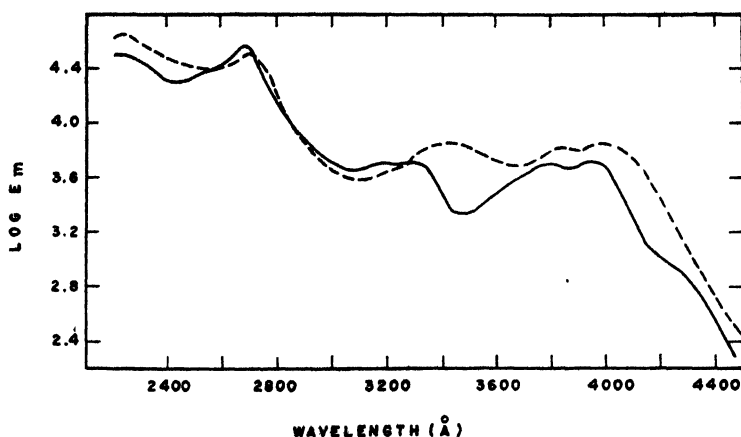
^a ii Compound synthesized by F. Bergmann and J. Szmuszkovicz.^b The more pronounced inflections are indicated by figures in parentheses.^c The spectra in n-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

TABLE I—*Concluded*WAVE LENGTHS AND INTENSITIES OF THE ABSORPTION MAXIMA—*Concluded*

Compound	Solvent ^a	Source ^a	Position of absorption maxima ^b	
			Wave length, Å	Intensity log <i>E</i> molar
1-Phenylnaphthalene-2,3-dicarboxylic acid anhydride	1,4-Dioxane	iii	2580	4.74
			3000	3.80
			3100	3.80
			3440	3.57
			3580	3.70
	Ethanol		2280	4.65
			2400	4.73
			(2700)	3.70
			2850	3.80
			3240	3.20
			3380	3.26

^a iii. Compound synthesized by E. Bergmann.^b The more pronounced inflections are indicated by figures in parentheses.^c The spectra in *n*-heptane or dioxane solution were always quite similar. Major differences occur on solution in ethanol (see page 440).

The introduction of a methoxy group at position 7 significantly alters the spectrum (Curve 10-*a*). Both the A and C band groups are displaced bathochromically, although the B bands are hardly affected. The introduction

FIG. 10. 10-*a* ——— 7-Methoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane)10-*b* - - - - 4',7-Dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (dioxane) [XIV]

of a second methoxyl group in the 4',7-dimethoxy derivative has a slight additional influence on the A and C bands and also displaces the B bands (Curve 10-*b*). In both of these methoxy derivatives ethanolysis causes a reversion

to a spectrum like that of the ethanolysis product of the nonmethoxylated compound (Curves 11-a, 11-b, 11-c).

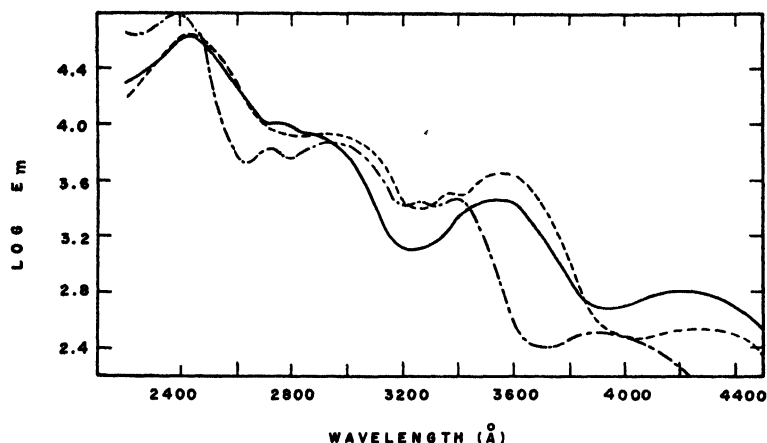


FIG. 11. 11-a ——— 7-Methoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (ethanol)
 11-b - - - - 4',7-Dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (ethanol)
 11-c - · - · - 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (ethanol)

In 6,7-dimethoxynaphthalene-1,2-dicarboxylic acid anhydride (XIV), introduction of the 6-methoxy group causes the absorption bands to shift *hypsochromically* (12-a); the methoxyl groups at 6 and 7 seem to exercise opposing

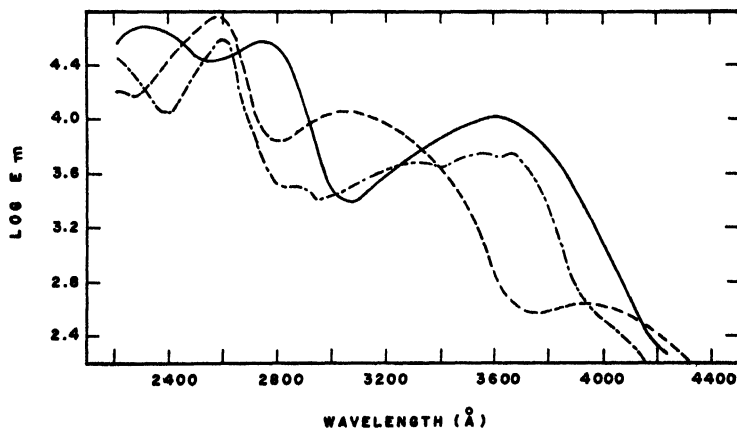
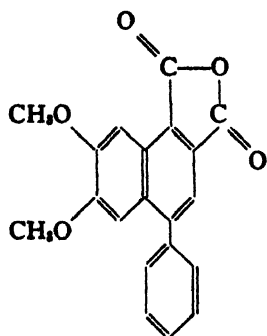


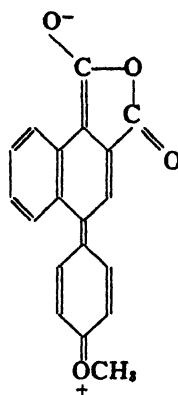
FIG. 12. 12-a ——— 6,7-Dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (dioxane)
 12-b - - - - Ditto. (ethanol)
 12-c - · - · - 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (*n*-heptane) [I]

influences. Methoxy groups at 4' and 7 may exert their major effect through the participation in the resonance of structures typified by XV and XVI, in which the negative charge is on the carbonyl oxygen atom at position 1.

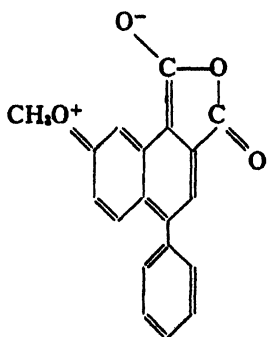
Such quinonoid structures cannot be written for 4'- and 7-methoxy derivatives in which the charge is transferred to the carbonyl oxygen atom at 2. In the case of the 6-methoxy compound the opposite is the case (XVII). In the 6,7-dimethoxy derivative there is, therefore, a competitive action between the stabilizing effects of the two methoxyl groups on the two carbonyl groups, and the abnormal effects on the spectrum may result from this crossed conjugation.



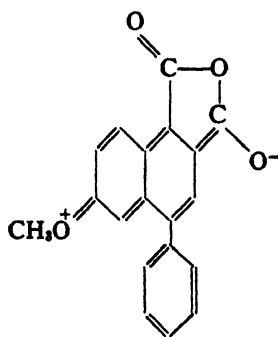
XIV



XV



XVI



XVII

V. OTHER ARYL DERIVATIVES OF NAPHTHALENE-1,2-DICARBOXYLIC ANHYDRIDE

The spectra of 4,7-diphenylnaphthalene-1-carboxylic acid (XVIII) and the corresponding hydrocarbon (XIX) are compared in Curves 13-a and 13-b. The spectrum of the hydrocarbon resembles that of 2-phenylnaphthalene (13-c) but the introduction of the 1-carboxyl group produces a broad new band extending into the visible region of the spectrum. Conjugated substituents at 4 and 7 will exercise a reinforcing action on the 1-quinonoid excited states (cf. XV, XVI) and steric inhibition of resonance will be slight in the

absence of substituents at 2 and 6. These conditions are favorable for the stabilization of the excited states of the 1-carboxylic acid, and the long wave absorption band is understandable.

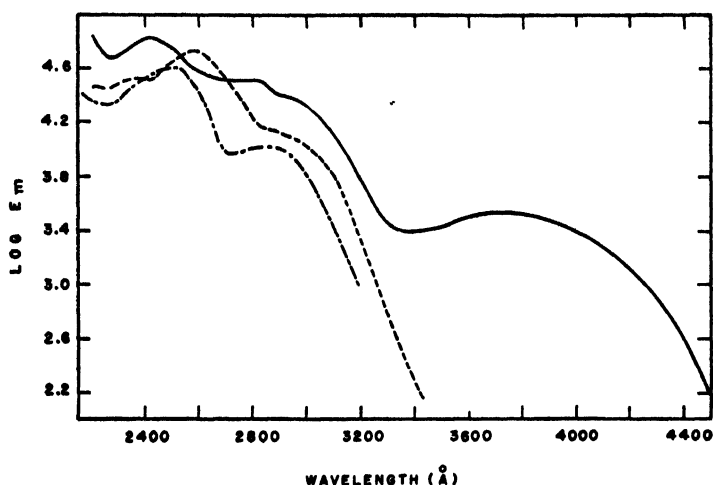
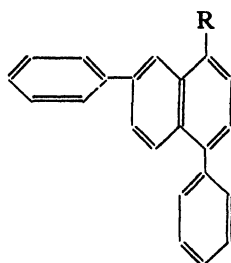


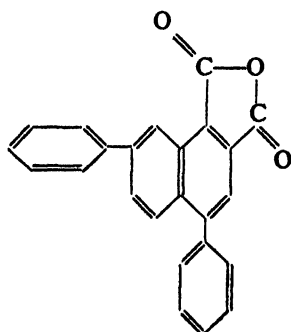
FIG. 13. 13-a ——— 4,7-Diphenylnaphthalene-1-carboxylic acid (ethanol) [XVIII]
 13-b - - - - 1,6-Diphenylnaphthalene (ethanol) [XIX]
 13-c - · - · - 2-Phenylnaphthalene (ethanol)



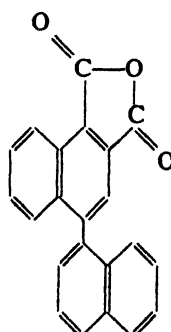
XVIII (R = -COOH)

XIX (R = -H)

If the 1-carboxylic acid group is replaced by the 1,2-dicarboxylic acid anhydride ring (XX) Curve 14-a is obtained, and on ethanolysis the spectrum shifts hypsochromically (14-b).



XX



XXI

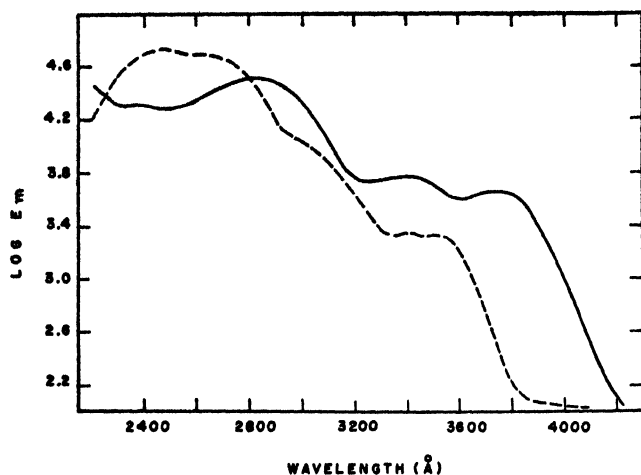


FIG. 14. 14-a ——— 4,7-Diphenylnaphthalene-1,2-dicarboxylic acid anhydride (dioxane) [XX]
 14-b - - - - - *Ditto.* (ethanol)

The spectrum of 4,1'-dinaphthyl-1,2-dicarboxylic acid anhydride (XXI) shown in Curve 15-a is quite similar to that of I (15-b), and the spectra of the corresponding ethanolysis products are also similar (16-a, 16-b).

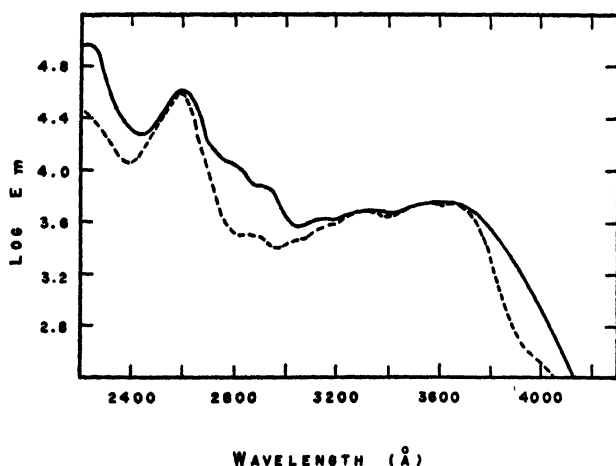


FIG. 15. 15-a ——— 4,1'-Dinaphthyl-1,2-dicarboxylic acid anhydride (dioxane) [XXI]
 15-b - - - - - 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (n-heptane) [I]

VI. DERIVATIVES OF NAPHTHALENE-2,3-DICARBOXYLIC ACID ANHYDRIDE

The spectrum of naphthalene-2,3-dicarboxylic acid anhydride (X) has been discussed in Section I. The introduction of the 1-phenyl group (XXII) greatly diminishes the fine structure (Curve 17-a) and displaces the B band group by 150 Å; the spectra of the ethanolysis products of both compounds are alike (18-a, 18-b).

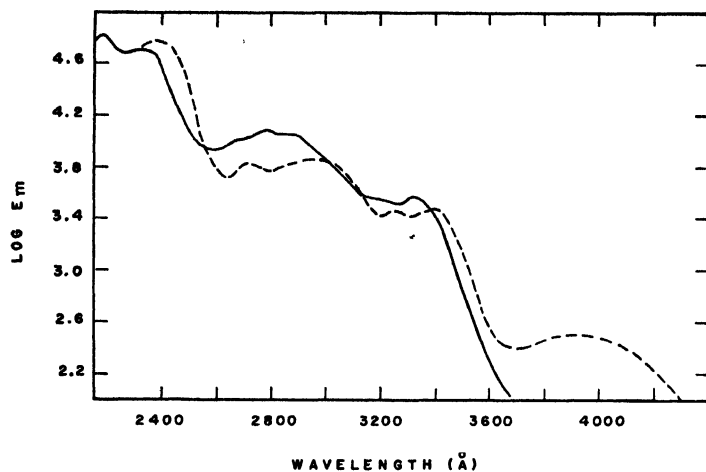


FIG. 16. 16-a ——— 4,1'-Dinaphthyl-1,2-dicarboxylic acid anhydride (ethanol)
 16-b - - - - 4-Phenylnaphthalene-1,2-dicarboxylic acid anhydride (ethanol)

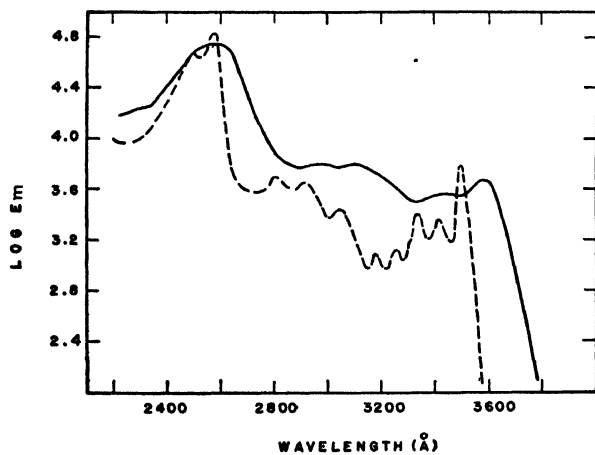


FIG. 17. 17-a ——— 1-Phenylnaphthalene-2,3-dicarboxylic acid anhydride (dioxane) [XXII]
 17-b - - - - Naphthalene-2,3-dicarboxylic acid anhydride (n-heptane) [X]

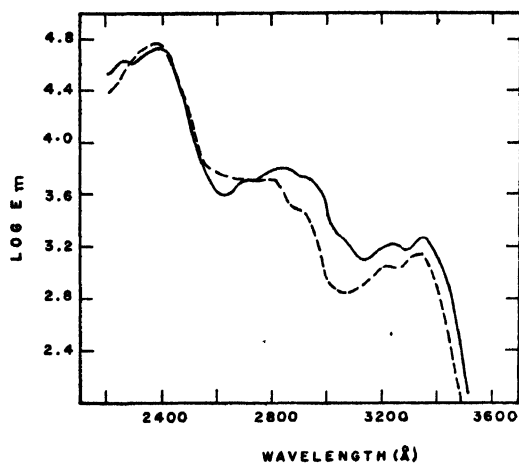
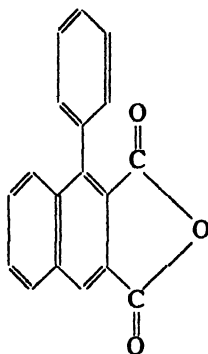


FIG. 18. 18-a ——— 1-Phenylnaphthalene-2,3-dicarboxylic acid anhydride (ethanol)
 18-b - - - - Naphthalene-2,3-dicarboxylic acid anhydride (ethanol)

In this series of compounds it seems that provided the anhydride ring is present the phenyl substituent couples strongly with the naphthalene ring system, but this effect is depressed on reaction with ethanol.



XXII

Discussion

As yet, the quantum mechanical analysis of the electronic levels of organic compounds has not been developed sufficiently to provide a rigid interpretation of the ultraviolet absorption spectra of such complex molecules as are considered here. The recent work of Coulson (4), Mullikan (14, 15), Walsh (23), Pullman, Pullman, and Daudel (5, 6, 16, 17), and others, however, indicates that considerable progress is being made in this direction.

One of the primary objects of this paper, as of earlier papers from this laboratory (8, 9, 10), is to present spectrographic data on complex compounds, and to draw attention to certain empirical relationships between the spectra and the molecular structure which are of value in the elucidation of molecular structure and which must eventually be brought within the framework of the quantum mechanical treatment.

To this end, it is convenient to make use of quasi-classical concepts of the process of electronic excitation, in order to provide a basis for the orderly and rational presentation of the data and to emphasize certain correlations between spectra and molecular structure. It is not considered to be a matter of undue concern if on the basis of these simple concepts the interpretation lacks completeness or even leads to occasional inconsistencies.

For the purpose of description, the naphthalene spectrum has been divided into three groups of bands, designated A, B, and C, and there can be little doubt that, in naphthalene itself, these correspond to three separate states of electronic excitation.* In the simpler derivatives the same three groups of bands are clearly to be distinguished. In the more highly substituted compounds the description of the spectra in terms of A, B, and C regions is

* The electronic states associated with the various regions of the naphthalene spectrum have been described also by West (24).

retained as a matter of convenience, but it is by no means certain that these separate parts of the spectrum bear much more than a formal relation to the three well defined regions of the naphthalene spectrum. This comment applies particularly to the C region.

The postulate of Scheibe (18, 19) and of Lewis and Calvin (12) that the directions of electronic excitation in the plane of the molecule can be resolved into orthogonal vectors giving rise to x -bands and y -bands has been used previously in interpreting the effects of substituents on the spectrum of anthracene (10). In the naphthalene compounds discussed here, distinctions between the effects of the introduction of conjugated substituents at positions 1 and 2 can be explained in terms of the orientation of the exciting polarization provided the conjugated substituents are small, but the picture gets confused when the conjugation becomes more extensive as in the 1- and 2-naphthal-acetones.

In the unsubstituted naphthalene molecule, considerations of symmetry would require the directions of such oriented polarization vectors to correspond closely with the symmetry axes in the plane of the molecule. Since the direction of the dipole in the 1-amino group lies along the bb' -axis (II), its primary effect will be restricted to the excitation of the B band. In more complex substituents, where the symmetry in the plane of the molecule is diminished by the extension of the conjugated chain, it is not possible to postulate the directions of x -band and y -band excitation from considerations of molecular geometry alone. In the general case the dipole moment of the substituent will have components in the directions of both the aa' - and bb' -axes, and any change in the conjugated substituents is liable to alter both the magnitude and the direction of the exciting polarization vectors. Therefore, it is only for small substituents, in molecules possessing a high degree of symmetry, that this analysis of substituent effects in terms of x -bands and y -bands can be applied effectively.

Another guiding principle that has aided in the rational interpretation of these substitution effects is the steric inhibition of resonance. In several instances (e.g., 9,10-diphenylanthracene) it has been clearly established that this effect may be sufficiently strong to inhibit completely any interaction between the aromatic ring and a potentially conjugatable substituent.

In the naphthalene series, it would appear that steric inhibition of resonance is more or less complete for the 1-substituted carboxy group, provided a second carboxy group, or other large substituent, is present at the vicinal 2-position. In the absence of a large substituent at 2, the naphthalene-1-carboxyl system is hindered only slightly.

A further factor influencing these substitution effects is the mutual reinforcing or antagonistic actions of two or more substituents in the same molecule. Such an antagonistic action has been postulated to account for the

differences in the spectra of 7-methoxy and 6,7-dimethoxy-4-phenylnaphthalene-1,2-dicarboxylic acid anhydride. This type of effect warrants further investigation in simpler compounds amenable to an analysis of the electron density distribution by the method of Pullman, Pullman, and Daudel.

In addition to these specific effects, the introduction of a substituent tends to shift the whole spectrum to longer wave lengths (B effect). This is seen most clearly following the introduction of alkyl substituents at positions where they do not increase steric inhibition of resonance. There is both experimental (10) and theoretical evidence (22) to indicate that this B effect acts primarily by raising the ground state of the molecule and it tends to produce a bodily shift of the whole spectrum. In the majority of the naphthalene compounds discussed here this effect is masked by conjugation effects, but it is seen in the alkyl and halogen derivatives of 4-phenylnaphthalene-1,2-dicarboxylic acid anhydride (Curve 9-a).

Experimental

The majority of the compounds discussed in this paper were prepared at the Daniel Sieff Research Institute and the methods of synthesis and proofs of structure have been described elsewhere (2, 3, 21). The spectra were determined on a Beckman model DU spectrophotometer using a constant band width of 10 Å.

Acknowledgment

We wish to express our indebtedness to Drs. E. Bergmann, F. Bergmann, and J. Szmuszkowicz who kindly placed at our disposal the majority of the compounds on which these studies are based. We also wish to thank Mr. A. Cahn, Miss Kathleen McLean, Miss M. Russell, and Miss L. Groth for technical assistance in the measurement of the spectra.

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

II. NITROLYSIS OF 1,5-ENDOMETHYLENE-3,7-DINITRO-1,3,5,7-TETRAZACYCLOOCTANE (DPT)¹

By A. F. MCKAY, H. H. RICHMOND², and GEORGE F WRIGHT

Abstract

When 1,5-*endomethylene*-3,7-dinitro-1,3,5,7-tetrazacyclooctane (DPT) is nitrolyzed with nitric acid - ammonium nitrate mixture the products are cyclic trimeric and tetrameric methylenenitramines (RDX and HMX). When the ammonium nitrate in this nitrolysis mixture is replaced by anhydrides such as nitrogen pentoxide or acetic anhydride then terminally esterified linear polymethylenenitramines such as 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanone and the 1,9-diacetoxy analogue respectively are obtained. Replacement of this nitric acid - anhydride mixture by acetyl nitrate does not produce the same type of nitrolysis. It is therefore concluded that nitric acid and an anhydride act independently, the former as a nitrolyzing agent and the latter as an esterifying agent. Alternatively the presence of ammonium nitrate serves to promote esterification and/or promote demethylation.

The preparation of 1,5-*endomethylene*-3,7-dinitro-1,3,5,7-tetrazacyclooctane (DPT) in anhydrous medium has been described (3) as a double scission at the amine nitrate linkages of hexamethylenetetramine (hexamine) dinitrate. The reaction conditions are mild and the amount of nitrolyzing acid is limited (to 2 equivalents). The resulting DPT is by no means stable to nitric acid. This report describes the subsequent scissions that it undergoes.

The dual nitrolysis in 99.6% nitric acid at 25° C. at the *endomethylene* linkage A,A' has been described (3). No isolable product could be discovered when DPT was heated to 70°-75° C. with 99.6% nitric acid, but the milder reagent ammonium nitrate - nitric acid (1 : 1.78 molar) produced a mixture of Cyclonite (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). According to thermal analysis of this mixture, the yields approximated 52% RDX and 17% HMX. When the ammonium nitrate - nitric acid ratio was 1 : 1, the RDX yield was slightly higher (57%) while the HMX yield became lower. The mode by which the two products are evolved is shown in the following formulation as scission at A,A' to produce HMX or scission at B,B' to produce Cyclonite (RDX).

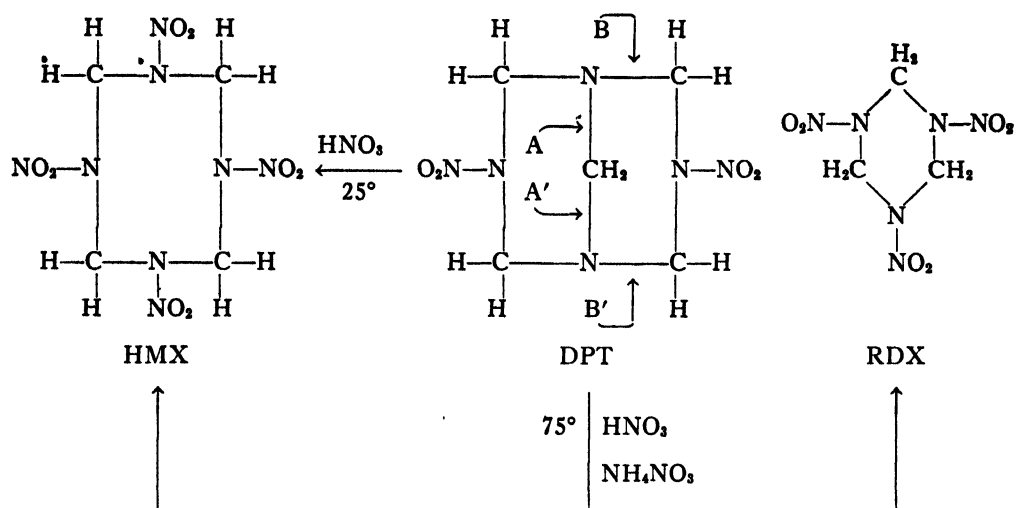
When nitric acid containing nitrogen pentoxide was treated with DPT at 0° to 25° C. a linear compound, 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanone, III, was obtained on dilution. Evidence for this structure is furnished by replacement of the nitroxy groups by methoxy or ethoxy radicals. This conversion of nitrate ester to alkyl ether is novel and specific for esterified amino methylols. It is remindful of the ester interchange recently reported (3), between dinitroxy and diacetoxy dimethylnitramide. The nitrate ester

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III also undergoes this ester interchange with sodium acetate in acetic acid to give 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, II. This further substantiates the structure of III because it provides an acetyl analysis.



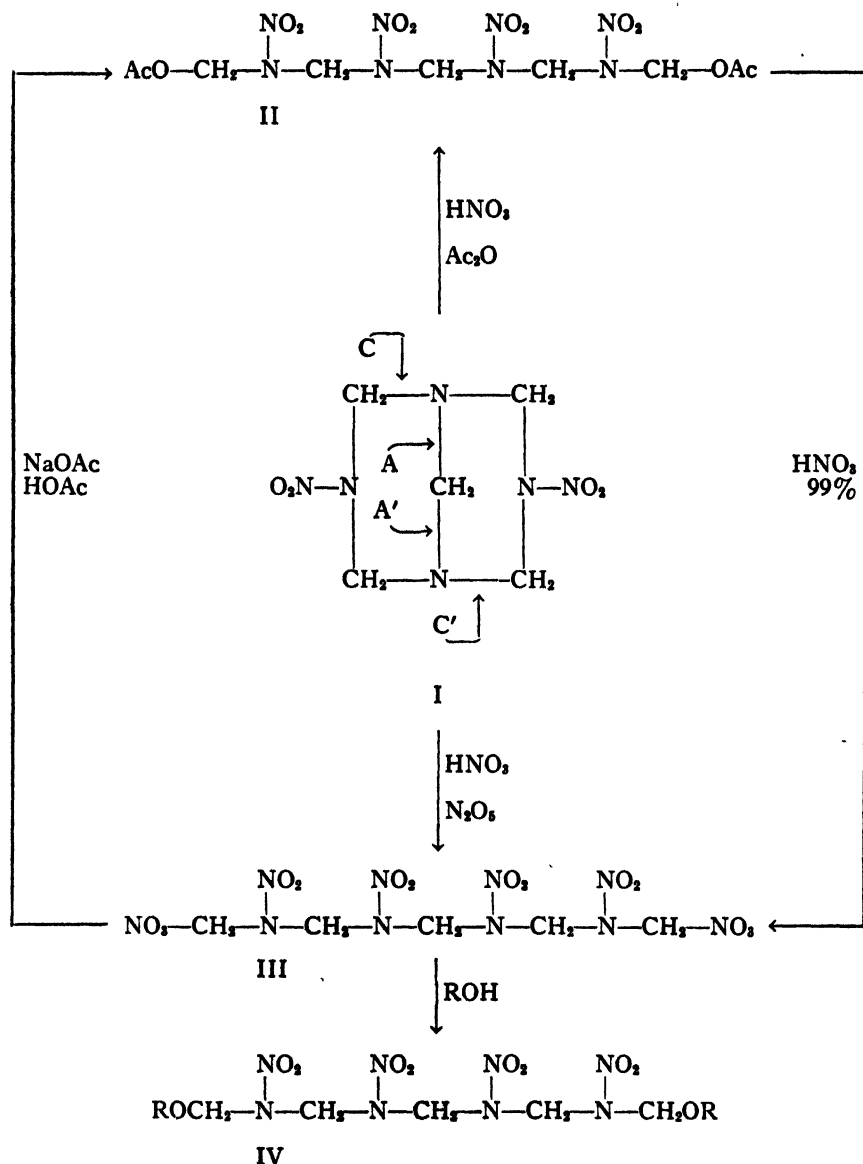
The acetate ester II can be produced directly and in good yield from DPT if the latter compound is treated at 44° C. with a mixture of acetic anhydride and nitric acid. It will ester-interchange in nitric acid solution to the dinitroxy compound III, and the two-step reaction is preferred for preparation of III because it obviates the requirement for nitrogen pentoxide.

The yield of 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazacyclononane, II, is slightly better at 44° C. than at 65° C. but the course of the reaction at the higher temperature is the same. If ammonium nitrate is added to the nitric acid - acetic anhydride system, with which DPT is treated at 65° to 70° C. then the chief product is HMX. It is impure, and may be contaminated with 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, II, but when it is purified from boiling nitric acid a 65% yield of good quality HMX is obtained.

It has been fashionable to consider a mixture of acetic anhydride and nitric acid as a source of acetyl nitrate, the ester being considered as the active agent. Evidence is accumulating, however, to indicate that acetyl nitrate is not active in such a mixture (4). Indeed the equilibrium $\text{AcONO}_2 + \text{HOAc} \rightarrow \text{Ac}_2\text{O} + \text{HNO}_3$ seems to be far to the right. This has been tested in the procedure for conversion of hexamine to 1,5-dinitro-3,7-endomethylene-1,3,5,7-tetrazacyclooctane (DPT) (3) by replacing nitric acid with acetyl nitrate. In those experiments where acetic acid was present, DPT was obtained, although the yield was dependent on the amount of this acid used. However, when chloroform or acetic anhydride was used as the solution medium, only hexamine dinitrate could be discovered at the end of the reaction.

The significance of acetyl nitrate was also tested by repetition of the nitrolysis of hexamine to 1,9-diacetoxy-4-aceto-2,6,8-trinitro-2,4,6,8-tetrazanonane (2). When acetic acid was present a 16% yield was obtained,

almost identical with that obtained when acetic anhydride and nitric acid were used. Replacement of the acetic acid by acetic anhydride reduced the yield to 3%. This small yield was undoubtedly owing to the presence of



some acetic acid in the anhydride, since when either acetic acid or its anhydride was replaced by chloroform, none of the diacetoxyacetotrininitrotetrazanonane was obtained.

There seems then to be no evidence that acetyl nitrate acts as a nitrolyzing agent except when it has been converted by acetic acid to nitric acid and acetic anhydride. In the present discussion, this nitric acid - acetic anhydride mixture like nitrogen pentoxide in nitric acid, is considered a simple solution

wherein absence of water has appreciably reduced the acidity of the nitric acid. In both instances nitric acid is considered as the nitrolyzing agent, while acetic anhydride or nitrogen pentoxide are considered as esterifying agents.

In order to form the linear compounds II and III a different pair of scissions must occur than could be specified for the cyclic compounds HMX and Cyclonite (RDX). There are only two possibilities if structures are excluded in which two nitro groups are attached to one amino nitrogen, and no such compound has ever been reported. Either a symmetrical scission at C and C' may occur, or else an unsymmetrical scission at A' and C. No phase of the present work can suggest a choice, but Bachmann's conversion (1) of 1-acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane (the intermediate he isolated in conversion of DPT to HMX) to the acetate ester II strongly suggests the unsymmetrical scission A' and C.

On this basis, the weakest linkage during nitrolysis is probably a bridge-link; subsequently the choice may depend on the rapidity and completeness with which the free hydroxyl group is esterified. If, following scission at A', the pendant hydroxyl group remains free for an appreciable time, the subsequent split is at A, and liberation of formaldehyde accompanies the nitration. If the hydroxyl group is esterified, however, then the linkage A is strengthened, and subsequent scission will occur at the only available linkage, C.

If esterification alters the reaction to favor formation of the linear compounds, then the production of HMX instead of 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane when ammonium nitrate is present in the acetic anhydride-nitric acid solution must mean either that ammonium nitrate facilitates formaldehyde removal (demethylation) or else hinders esterification.

The effects are probably intercorrelated. Thus, it is known that, when ammonium nitrate is dissolved in the medium, the reaction temperature must be raised to 60°-70° C. before the nitric acid is effective either for esterification or nitrolysis. This higher temperature undoubtedly promotes demethylation. The freed formaldehyde can then be stabilized by methylamine formation with the ammonium nitrate which is present in the medium.

Experimental*

1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, II

To a stirred solution of 20 gm. (0.091 mole) DPT, I, in 438 cc. (4.66 moles) of acetic anhydride, was added 140 cc. (3.34 moles) of 99.6% nitric acid over 40 min. at 44° C. The mixture was then cooled to 15° C. and poured on ice. The filtered precipitate was washed with ethanol and air-dried to yield 31.7 gm., m.p. 176° to 185° C., or 87% of theoretical. Three crystallizations from

* All melting points are corrected against reliable standards.

nitromethane or, better, from acetone raised this to 186.5°–187.2° C. Calc. for $C_9H_{16}N_8O_{12}$: C, 25.2; H, 3.76; N, 26.2; CH_3CO , 19.8%. Found: C, 25.3; H, 3.93; N, 26.2; CH_3CO , 20.3%.

The acetyl determination was complete in one hour, thus indicating absence of the $N-COCH_3$ linkage. The high hydrogen result is characteristic of these unstable nitramines when the sample is burned without admixture with potassium dichromate. The compound is destroyed (82%) by one hour's reflux with boiling aqueous ammonia. The evaporated solution gives a positive lanthanum nitrate test (5) for acetic acid.

The compound gives a strong Franchimont test for the nitramine linkage. Its melting point is not depressed by the analogous nitrate ester, III (solid solution?). It is oxidized after 18 min. by 70% nitric at 25° C., but immediate dilution yields a compound melting poorly at 202° C. which has not been identified. It is neither Cyclonite nor III.

The substance can also be prepared from 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, III. A solution of 0.3 gm. (7×10^{-4} mole) of III with 0.23 gm. sodium acetate in 5 cc. of acetic acid was boiled for three minutes, then cooled, filtered, and the precipitate washed with water. It weighed 0.2 gm. (70% of theoretical) and melted at 183° C. When Cyclonite was treated similarly it was recovered unchanged, thus indicating that the nitramino group is unaffected by such treatment.

1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, III

When 150 gm. (0.36 mole) of pure diacetoxo compound II (m.p. 185° C.) was added to 1 liter (24 moles) of 99.6% nitric acid at 0° C., and the reaction mixture after 15 min. at 25° C. was poured into ice, a precipitate was formed. It weighed 153 gm. and melted at 202° to 203° C. This 98% yield was thrice crystallized from nitromethane to melt at 204.5° to 205° C., when the sample was introduced at 190° C. and heated rapidly. Less pure II gives an inferior product. Only 20% of the compound was destroyed in 70% nitric acid at 25° C. for 30 hr., but rapid decomposition occurred when the nitric acid was boiled. Calc. for $C_8H_{10}N_{10}O_{14}$: C, 13.8; H, 2.30; N, 32.3%. Found: C, 13.8; H, 2.43; N, 32.3%.

This compound is a powerful explosive (Trauzl block expansion $2.2 \times$ TNT at bulk density 0.69). It is 12 times as sensitive to impact as TNT.

The same compound is obtained when DPT is treated with nitric acid containing enough nitrogen pentoxide to give an apparent titration of 106% HNO_3 (1.8 gm. 100% HNO_3 per gram N_2O_5). Ten grams (0.046 mole) of DPT was added to 63 cc. (1.6 moles) of stirred 106% nitric acid over 35 min. at 20° C. After a total time of 50 min. the whole was drowned in ice, filtered, water washed, and air-dried. The yield of 13.4 gm. (72% of theoretical) melted at 191° to 193° C. Three crystallizations from nitromethane raised this to 202° C.

1,9-Dimethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, IV. (R = CH₃)

When 0.2 gm. (4.6×10^{-4} mole) of the nitrate ester, III, was boiled in 10 cc. methanol for 10 hr., a compound crystallized out on cooling. When filtered and washed with methanol, it weighed 0.16 gm. and melted at 177° to 183° C. This 93% yield was crystallized from 1 : 1 dioxane-methanol to melt at 182° to 183° C. Calc. for C₇H₁₈N₈O₁₀ : C, 22.6; H, 4.32; N, 30.8%. Found: C, 22.5; H, 4.27; N, 30.7%.

1,9-Diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, IV (R = C₂H₅)

A procedure identical with the above gave a 43% yield of product, m.p. 166° to 167° C. The melting point was not raised by 1 : 1 ethanol-dioxane crystallization. Calc. for C₉H₂₀N₈O₁₀ : C, 27.0; H, 5.04; N, 28.0%. Found: C, 27.4; H, 4.94; N, 28.2%.

1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX)

A mixture of 10 gm. (0.046 mole) of DPT (m.p. 203° to 204° C.) and 46.2 cc. (0.394 mole) of acetic anhydride was stirred at 65° to 70° C. (bath 60° C.) while a solution of 11.1 gm. (0.138 mole) of ammonium nitrate in 13.4 cc. (0.319 mole) of 99.6% nitric acid was added over a 15 min. period. The suspension dissolved and then reappeared. After subsequent stirring for 22 min. and 10 min. at 25° C., the whole was poured into 400 gm. of ice and water. The filtered solid, washed with 300 cc. water and air-dried, weighed 14.8 gm., m.p. 226° to 250° C. It was boiled with 207 cc. of 70% nitric acid until strong nitrogen oxide evolution commenced. After cooling and drowning with 2 liters water, it was filtered and dried at 70° C. to weigh 8.9 gm. (65.5% of theoretical) with melting point 267° to 268° C.

Cyclonite-HMX Mixture from DPT

A stirred solution of 1.1 gm. (0.014 mole) of ammonium nitrate in 1.3 cc. (0.031 mole) of 99.6% nitric acid was heated to 70°–75° C. in a water bath while 0.200 gm. (9×10^{-4} mole) of DPT was added. After 15 min. the mixture was drowned in ice and water, filtered, and the precipitate washed and dried. It weighed 0.15 gm. and melted at 187.5° to 189.5° C. According to thermal analysis by the melting point composition diagram to be reported in the next paper of this series, this contained about 30% HMX, which would constitute a 17% yield; the remainder, if Cyclonite, would be 52% of the theoretical both on the 1 : 1 basis. Fractional crystallization from nitromethane yielded these two, and no other, compounds.

This ratio of HMX to RDX was shifted by decrease in amount of nitric acid (34 moles to 20 moles) and increase of ammonium nitrate to quantity equimolar with the acid. A solution of 126 gm. of 99.6% nitric (2 moles) and 160 gm. (2 moles) of ammonium nitrate was stirred at 68° C. while 21.8 gm. (0.1 mole) of DPT was added over 20 min. After 30 min. more at this temperature, the mixture was drowned in ice and water and filtered. The product melted at 197° to 202° C. and weighed 13 gm. and, according to

thermal analysis, contained about 3% HMX. The yields are therefore 1.77% HMX and 57% Cyclonite. Neutralization of the liquors produced only a trace (less than 0.15%) of impure DPT.

When hexamine was subjected to exactly these same reaction conditions a good Cyclonite (m.p. 202° to 203° C.) was obtained in 19% yield after purification from hot 70% nitric acid. Neutralization of the reaction liquors precipitated a 17% yield of DPT on the equimolar hexamine basis.

Attempted Formation of DPT and 1,9-Diacetoxy-4-aceto-2,6,8-trinitro-2,4,6,8-tetrazacyclooctane, XVI, with Acetyl Nitrate

The acetyl nitrate was prepared by the method of Pictet and Khotinsky (6); it boiled at 38° to 43° C. (15 mm.). The procedures wherein this reagent replaced nitric acid – acetic anhydride were otherwise identical with those reported elsewhere (2, 3) except when chloroform was used in the preparation of DPT (Expt. 4, Table I). In this instance a gummy solid precipitated from the chloroform solution. This seemed to be a complex of the type which acetyl nitrate forms with pyridine. It was intractable until it was dissolved in aqueous acetic acid, from which hexamine dinitrate was precipitated. The proportions and yields are indicated in Table I.

TABLE I

Expt. No	Moles hexamine	Moles HOAc	CHCl ₃ , cc.	Moles HNO ₃ 99%	Moles Ac ₂ O	Moles AcNO ₃	Product
1	0.014	0.688	15	0.048	0.024	0.028	DPT, m.p. 204° C. Yield, 36%
2	0.014	0.145			0.024	0.028	DPT, m.p. 199° C. Yield, 12%
3	0.015					0.029	Hexamine dinitrate, Yield, 66%
4	0.015				0.106	0.029	Hexamine dinitrate, Yield, 21%
5	0.014	0.13	15	0.048	0.01	0.048	XVI, m.p. 148° to 151° C. Yield, 16%
6	0.014	0.13			0.058		XVI, m.p. 146° to 148° C. Yield, 15%
7	0.014				0.01	0.048	XVI, m.p. 149° to 150° C. Yield, 3%
8	0.014					0.048	No water-insoluble product

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

III. PREPARATION OF PURE CYCLONITE¹

By F. J. BROCKMAN, D. C. DOWNING,² AND GEORGE F WRIGHT

Abstract

All Cyclonite prepared by nitrolysis of hexamethylenetetramine has been found to contain 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). This impurity is not present in Cyclonite prepared by oxidation of 1,3,5-trinitroso-1,3,5-triazacyclohexane. The oxidation yields 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane as an intermediate. There seems then to be a difference in reactivity of two of the three aza linkages in triazacyclohexanes.

When Cyclonite is prepared from hexamethylenetetramine (hexamine) with nitric acid containing acetic anhydride (1, 4), it always contains 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, HMX, as an impurity. The extent of this impurity can be estimated by thermal analysis according to the melting point – composition diagram shown in Fig. 1. The lower line of this diagram represents the first observable softening of the sample, while the top line records the disappearance of the last crystal.

Cyclonite prepared by the method of Hale (2) ordinarily melts at 202° to 203.5° C. after it has been boiled with nitric acid. According to Fig. 1 it ought then to contain less than 1% of impurity. Although the impurity cannot be detected by microscopic crystallographic examination it must necessarily be present, because repeated wasteful crystallization of Cyclonite from acetic acid finally raises the melting point to a constant value of 204.5° to 205° C.

Confirmation that this impurity was HMX was obtained during an inspection of one of the wartime plants which manufactured Cyclonite by the Hale method. A scaly deposit on the apron of a classifier filter had formed where the diluted reaction mixture was cooled, and this turned out to be almost pure HMX (m. p. 269° C.). It must, therefore, be concluded that all Cyclonite prepared from hexamine contains HMX as an impurity; this impurity is difficult to remove because it is more stable and less soluble than Cyclonite.

In view of the uncertainty concerning purity of a substance which tends by its rapid crystallization to occlude impurities strongly, a method was sought whereby Cyclonite could be prepared otherwise than by nitrolysis of hexamine. It was found that this could be accomplished by oxidation of 1,3,5-trinitroso-1,3,5-triazacyclohexane, I.

The trinitroso compound, I, is prepared from hexamine (3) in aqueous solution. Although it is not very stable it can be purified with ease from the impurity 1,5-*endomethylene*-3,7-dinitroso-1,3,5,7-tetrazacyclooctane, which is formed at the same time. The trinitrosotriazacyclohexane, I, reacts

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Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.

² Holder of a Studentship under the National Research Council of Canada, 1941-42.

violently with strong nitric acid at room temperature, usually with inflammation, but it does not char at -40°C . if it is added to the strong acid in small portions.

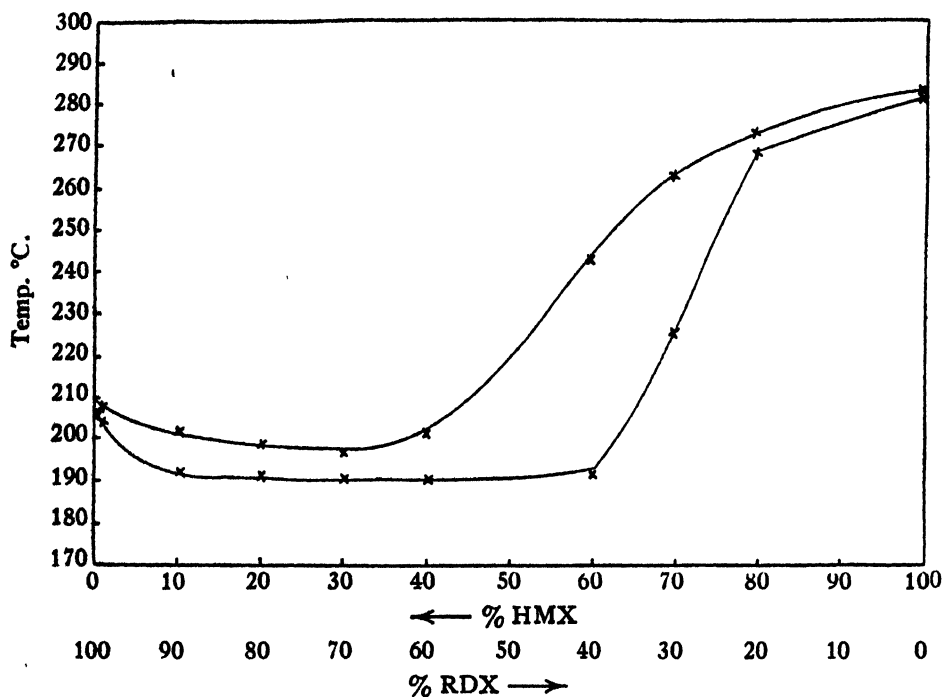


FIG. 1. Curve showing complete range of RDX-HMX mixed melting points.

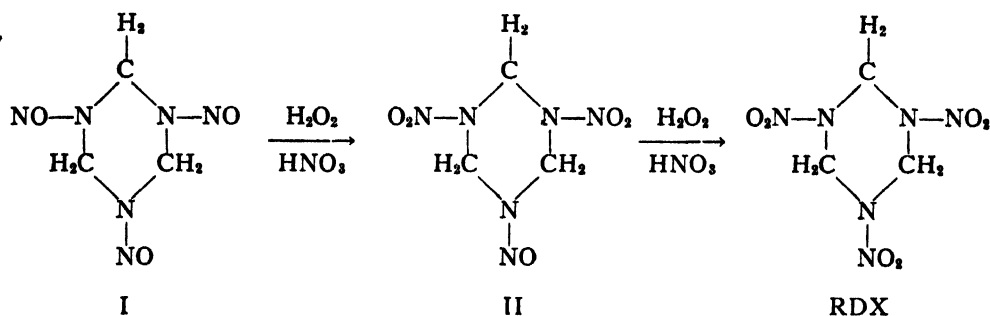
The oxidizing medium first used consisted of 82 equivalents of 99% nitric acid, 3 of hydrogen peroxide, and 3.7 of water (introduced with the peroxide, thus reducing the nitric acid concentration to 92–94%). This solution was chilled to -40°C . and one molar proportion of the trinitrosamine added carefully in small portions, with vigorous stirring. The reaction mixture probably absorbed water from the air during this addition.

When the clear reaction mixture at -40°C . was poured on to ice, a light yellow solid precipitated which was not Cyclonite. It gave positive Franchimont and Liebermann tests for nitro and nitroso groups, respectively, and it liberated iodine from acid potassium iodide, although more slowly than did the trinitrosamine, I. Cyclonite liberates almost no iodine from aqueous potassium iodide. When the product was returned to the same oxidizing mixture at -40°C . and the solution allowed to warm to room temperature, it was converted to very pure Cyclonite in good yield.

These properties, together with the analytical data, indicate that the compound II is 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane.

The compound II is contaminated with Cyclonite (RDX) but is sufficiently soluble in boiling water that it can be separated from this impurity, and no indication has been found that a mononitro-dinitroso analogue is present.

This indicates that when two nitro groups have been established in the cyclotrimethylenetriamine ring the third is introduced with somewhat more difficulty.



The isolation of dinitronitrosotriazacyclohexane, II, depends on relative reaction rate and not on deficiency of oxidizing agent. This may be shown by allowing the reaction mixture to stand overnight at -40°C . Dilution on ice yields 54% of the theoretical amount of Cyclonite (RDX) instead of the 49% yield of II which can be obtained if the reaction solution is drowned shortly after addition is complete. If, alternatively, when addition at -40°C . is complete, the solution is at once allowed to warm to room temperature, the product is pure Cyclonite and not II.

Reaction conditions indicating the optima are shown in Table I. It may be seen that the reaction may be carried out without hydrogen peroxide

TABLE I
SYNTHESIS OF CYCLONITE

Expt. No.	Equiv. HNO_3	Moles, I	Addn. time, min.	Equiv. 30% H_2O_2	Additional variation	Holding time, min. at			Yield crude RDX	
						-40°C .	0°C .	30°C .	%	M.p.
1	80	0.001	5	3	0	0	500	0	55	204.5
2	240	0.001	5	3	0	0	500	0	46	204
3	85	0.187	30	3	0	0	1000	0	65	205.0
4	85	0.187	30	3	0	0	1000	1000	67	203
5	85	0.011	15	0	3 eq. Na_2O_2	15	0	25	47	205
6	85	0.011	15	1.5	0	10	0	1000	64	205
7	85	0.011	15	0.75	0	10	0	1	66	205
8	85	0.011	15	0.75	0	10	0	60	66	205.0
9	85	0.011	15	0.75	0	10	0	1000	63	205.0
10	85	0.011	15	0.75	Run at 0°C .	0	0	120	10	205.0
11	85	0.011	15	0.75	Run at 0°C .	0	0	1000	12	205
12	85	0.011	15	0	0	0	0	10	66	202.5
13	85	0.011	15	0	0	0	0	1000	63	203.5
14	43	0.011	30	0	0	0	0	5	74	204
15	22	0.011	20	0	0	0	0	5	53	200
16	22	0.011	40	0	0	10	0	5	52	198.5
17	43	0.011	35	0	0.05 eq. AgNO_3	0	0	5	69	204.5
18	43	0.01	25	0	0.05 eq. V_2O_5	0	0	5	71	203
19	43	0.011	30	0	No water	0	0	5	48	202.5
20	43	0.011	35	0	No water	0	0	5	57	202.5

(Expts. 12 to 20) but the product is less pure. This may be owing to the beneficial effect of the water introduced in the peroxide. Van Romburgh (5) recommends 89% nitric acid for oxidation of dinitro-*p*-tolylmethylnitrosamine to the nitramine. Strictly anhydrous reaction conditions (Expts. 19 and 20) seem to give poorer product than was obtained from Expt. 14 under reaction conditions which were identical except for the exposure to atmospheric moisture.

The unusual purity of these crude products can be appreciated only after attempting to purify rigorously any Cyclonite prepared by nitrolysis of hexamine. The nature of the oxidation process may be expected to exclude possibility of eight-membered ring formation. The high purity is undoubtedly owing to absence of HMX.

Experimental*

Purification of Cyclonite

The best explosive-grade Cyclonite melts at 201.5° to 202.5° C. Cyclonite melting at 204.5° to 205.0° C., can be obtained by five crystallizations from acetic acid. In order to realize the high melting point, the product which crystallizes in massive crystals, extremely sensitive to impact, must be ground (under water) to crack open the faults and pockets which frequently occur. It is presumed that this acetic acid crystallization removes only 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) because this is the only other substance of the methyleneamine type which will resist oxidation by nitric acid. It is wise, prior to the acetic acid crystallization, to crystallize impure Cyclonite from boiling 70% nitric acid in an open flask.

1,3,5-Trinitroso-1,3,5-triazacyclohexane, I

To a stirred solution of 105 gm. (0.75 mole) hexamine in 1400 cc. water plus 600 gm. ice, in a 5 liter three-necked flask, was added an ice-cold solution from 340 cc. (4.1 moles) of concentrated hydrochloric acid and 1 kilo of ice. The acid solution was stirred while a solution of 250 gm. (3.6 moles) of sodium nitrite in 250 cc. water plus 150 gm. ice was added. The reaction mixture foamed up immediately; the foaming was controlled by air streams directed at the necks of the vessel. After one-half hour without stirring, the precipitate which had risen to the surface was filtered off, washed with water, and dried at 45° C. to give 61.1 gm. (26% on CH₂O basis) of pale yellow powder, m. p. 105° to 107° C. Of this, 60 gm. was crystallized from boiling ethanol (9 cc. per gm.) to give 48.8 gm., m. p. 105° to 107° C.; a second crop of 6.8 gm. was recovered on evaporating to 70 cc.

1-Nitroso-3,5-dinitro-1,3,5-triazacyclohexane, II

A solution was prepared by adding 3.9 cc. (ca. 0.035 mole) of 30% C. I. L. hydrogen peroxide dropwise to 41.5 cc. (62 gm., 0.99 mole) of 99% nitric

* All melting points are corrected against reliable standards. The heating rate for Cyclonite samples was 2° C. per minute.

acid stirred at -40°C . Stirring was continued at this temperature while 2.0 gm. (0.012 mole) of the powdered trinitrosamine was added in small portions over 15 min. No flashes of flame were observed, and only a little white fume. The clear yellow liquid was stirred for 30 min. longer at -40°C . and poured (still clear yellow with no sign of char) on 120 gm. of ice. The reaction mixture smelled of nitrous acid but not of formaldehyde. The light yellow solid which precipitated was filtered, and air-dried to weigh 1.12 gm. (45% of theoretical on basis of I \rightarrow II) and to melt at 125° to 137°C ., depending on rate of heating. Neutralization of the filtrate with ammonia to pH 5.6 yielded no trace of precipitate.

This compound is very soluble in acetone, nitromethane, and dioxane; quite soluble in chloroform and slightly less so in ethanol and benzene. Its solubility in water is less than in the above, but is quite appreciable. Crystallization from boiling benzene (50 cc. per gm.), and subsequently from boiling water (110 cc. per gm.), leaves much of the contaminant RDX undissolved. This material, m. p. 160° to 165°C ., is then finally purified by solution in a minimum of hot nitromethane. The RDX crop which separates on cooling is filtered off and the solution diluted with an equal volume of ether. The crystal crop thus obtained melts at 173° to 174°C .; repetition of this process yields a product melting at 176.6°C . (decomp.). Calc. for $\text{C}_3\text{H}_6\text{N}_6\text{O}_5$: C, 17.5; H, 2.91; N, 40.8%. Found: C, 17.6; H, 2.97; N, 40.5%.

In boiling mineral acids (for example, 15% nitric acid) it is decomposed with evolution of formaldehyde, easily detected by odor; on boiling with 10% sodium hydroxide a faint odor of ammonia is observable and a bromthymol blue test paper held in the mouth of the test tube is turned blue immediately. The compound gives a positive Franchimont test. In the Liebermann test it dissolves in cold concentrated sulphuric acid without immediate char or visible gassing and on addition of a phenol crystal does not change color; on warming, a green color develops. Cyclonite treated similarly develops a yellow color in the cold which goes to green on warming. The compound liberates iodine from aqueous potassium iodide faster than Cyclonite (which indeed does not appear to liberate iodine appreciably at room temperature) but much slower than trinitrosotrimethylenetriamine. In a semi-quantitative test, 0.02 gm. each of trinitrosotrimethylenetriamine, the oxidation product being investigated, and RDX, along with a blank control were each suspended in 2 cc. water plus 2 drops glacial acetic acid, and 0.10 gm. of solid potassium iodide added. The trinitrosamine tube was bright yellow in two minutes, the oxidation product pale yellow in 27 min., at which time the Cyclonite and blank tubes were each a barely perceptible yellow of intensity identical to the eye.

1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)

Dinitronitrosotriazacyclohexane, II, can be converted to RDX by further treatment with hydrogen peroxide - nitric acid. When 0.05 gm. of II was added at -40°C . to 0.10 cc. of 30% hydrogen peroxide in 1 cc. of 99% nitric

acid and the reaction allowed to warm to room temperature and maintained there for five minutes, 0.04 gm. (75% of theoretical) of very pure RDX, m. p 205°C ., was obtained by pouring the reaction mixture on 4 gm. of ice. A mixed melting point with purified RDX, m. p 204.5°C ., was not depressed.

The isolation of the intermediate is possible only when the cold reaction mixture (-40°C .) is poured on ice without being allowed to warm to room temperature. Thus the 45% yield described in preparation of II involved a 30 min. period at -40°C .; when the solution at this temperature was poured on ice immediately after addition was complete, the yield was 49%. When this reaction mixture was allowed to stand at 0°C . overnight, the product isolated after pouring on ice was a 54% yield of RDX, m. p. 205°C . When threefold quantities of hydrogen peroxide and nitric acid were used under these latter conditions, the yield was 45%.

The one-stage process standardized for the experiments listed in Table I consisted in addition of powdered I added (except in Expts. 19 and 20) to the strongly stirred nitric acid solution in a wide-mouth Erlenmeyer flask in a bath at -35° to -40°C . The Cyclonite was precipitated when the solution was poured into ice, filtered, ground, and dried at 100°C .

Oxidizing agents which failed to effect the conversion are: nitric acid – ammonium nitrate, nitric-phosphoric acids, nitric-acetic acids, nitric acid – acetic anhydride, camphor nitrate, tetranitromethane, Caro's acid, aqueous potassium chlorate, neutral hypochlorite, manganic acetate, ferric chloride, and nitric acid in nitromethane.

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PREPARATION AND EXTRACTION OF S^{35} ¹

By M. B. WILK

Abstract

Procedures are described for the preparation and extraction of carrier-free S^{35} , based on the $Cl^{35}(\pi, p)S^{35}$ reaction. Potassium chloride, sodium chloride, and ferric chloride have been used as target materials. The S^{35} is found to appear in a chemical form which exchanges rapidly with sulphate ion. Separation of S^{35} from irradiated potassium or sodium chloride is effected by taking advantage of the insolubility of these salts in aqueous hydrochloric acid solutions. Approximately 99.8% of the salt can be removed while leaving 95% of the S^{35} in solution. Separation from irradiated ferric chloride is effected by solvent extraction of the ferric chloride from aqueous 6 to 8 *M* hydrochloric acid solutions. Less than 0.1% of the total solids is left unextracted. The yield of S^{35} approaches 100%.

Introduction

Isotopes of Sulphur

The isotopic composition of natural sulphur is S^{32} —95.04%, S^{33} —0.74%, S^{34} —4.2%, S^{36} —0.016%. Three radioactive sulphur isotopes have been artificially prepared. S^{31} is a positron emitter of 3.2 sec. half life. S^{35} and S^{37} decay by β^- emission with half lives of 87.1 days and 5.04 sec. respectively (10).

It is apparent, therefore, that only S^{35} bears consideration for use as a radioactive tracer.

Properties of S^{35}

The existence of a long-lived radioisotope of sulphur was first observed by Andersen (1) on neutron irradiation of carbon tetrachloride. The mass assignment of S^{35} was made by Kamen (5) on the basis of cross section considerations. Kamen (5) reports a half life of 88 days, in good agreement with the value of 87.1 days published by Hendricks *et al* (3). No appreciable gamma activity has been found in the decay of S^{35} .

The β -ray spectrum of S^{35} was studied by Libby and Lee (8), who found a maximum energy of 107 ± 20 kev. Later work by Kamen (5) gave a value of 120 ± 15 kev. More recent values differ considerably from these. Solomon, Gould, and Anfinson (12) report a value of 167 ± 4 kev., closely corresponding to values obtained by the author. Overman (9), with a value of 170 kev. and Yaffe and Justus (16), with a value of 167 kev., confirm the higher value for maximum energy of β 's from S^{35} .

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Preparation of S^{35} by Means of a Chain-reacting Pile

Kamen (6) gives a summary of all known reactions which can be used to make S^{35} . While much of the early work with S^{35} was done with cyclotron-produced material, the primary source of the radioisotope at present is a chain-reacting pile. Only reactions using neutrons as the bombarding particle are discussed here.

On irradiation of sulphur with neutrons, S^{35} is formed by the reaction $S^{34}(n, \gamma)S^{35}$. This reaction occurs with thermal neutrons. The specific reaction cross section* is 0.26 barn† (2). However, the low abundance of S^{34} in natural sulphur reduces the natural atom cross section for formation of S^{35} to 0.011 barn.

Thus, even with irradiation to equilibrium at a flux of 5×10^{12} neutrons per cm.² per sec. (available in the N.R.X. pile) the maximum specific activity obtainable would be 0.028 millicuries (mc.) per mgm. In addition, contamination with radioactive P^{32} (1.7 Mev. β , 14.7 days half life), formed by $S^{32}(n, p)P^{32}$, occurs.

A more satisfactory method for preparing S^{35} is by the transmutation reaction $Cl^{35}(n, p)S^{35}$. This reaction occurs with thermal as well as fast neutrons (5). The specific reaction cross section for the thermal neutron reaction is given as 0.169 barn (2). Since the abundance of Cl^{35} in natural chlorine is 75.4% this means a natural atom cross section of 0.13 barn. Yields obtained in the N.R.X. pile were 10 to 20 times higher than this value would indicate. The discrepancy may be due to a resonance peak in the fast neutron range.

The thermal neutron capture cross section of chlorine is about 35 barns (11). The reactions which occur on pile irradiation of chlorine are shown in Table I.

TABLE I
REACTIONS OCCURRING ON NEUTRON IRRADIATION OF CHLORINE

Isotope	Reaction	Product	Half life	Energy, Mev.		Type neutron
				β	γ	
Cl^{35}	n, γ	Cl^{36}	1×10^4 yr.	0.66	None	Thermal
Cl^{35}	n, p	S^{35}	87.1 days	0.17	None	Thermal and fast
Cl^{35}	n, α	P^{32}	14.7 days	1.7	None	Fast
Cl^{37}	n, γ	Cl^{38}	37 min.	1.1, 2.8, 5.0	1.65, 2.15	Thermal

Because of its long half life, the Cl^{36} radioactivity developed is negligible if relatively short irradiation periods are used. Short-lived Cl^{38} decays in a day or so. Contamination by P^{32} is of the order of 1% of the total S^{35} , in terms of β particles emitted. The $P^{32} : S^{35}$ ratio can be reduced by (a) long

* Specific reaction cross section = cross section for neutron capture of natural sulphur \times isotopic abundance ratio of S^{34} .

† One barn = 10^{-28} cm.²

term irradiations, (b) irradiation in a thermal neutron flux, and (c) a long decay period.

The selection of an appropriate target material for production of S^{35} is governed by the following criteria: stability to heat and radiation, large proportion of chlorine, minimum interference by cation activity, ease of handling and extraction, chemical purity of material, and low neutron capture cross section of cation.

Early workers (1, 5) with S^{35} used carbon tetrachloride as a target material. While carbon tetrachloride offers the attractiveness of containing 92.2% chlorine, no interfering cation activity, and low neutron capture cross section of carbon, its instability to heat and radiation seriously limits its utility. More satisfactory targets are potassium, sodium, or ferric chlorides.

Experimental Work and Discussion

MEASUREMENT OF RADIATION FROM S^{35}

The very low energy of the β particles from S^{35} poses special problems as regards their quantitative detection. Fig. 1 shows a semilogarithmic plot of a typical external absorption curve obtained with a sample of substantially carrier-free S^{35} . This curve was obtained with a sample mounted on a very thin formvar film.* If the sample is mounted on a glass tray, the shape of the absorption curve obtained will differ somewhat, owing to differences in counting geometry and to the effect of backscattering.†

The bend in the absorption curve, together with the variation in the slope of the curve with counting geometry and backscattering effects, makes it difficult to characterize the S^{35} radiation by one external absorption half-thickness for the entire range.‡ For the particular case of a sample mounted on a thin film, using the initial portion of a linear plot (see Fig. 2), 4 mgm. per cm.² will cause a 50% decrease in counting rate.

The low energy of the radiation makes self-weakening a major problem. Experiments showed that samples of thickness 3 mgm. per cm.² will be weakened to the extent of 40% of the total activity. Internal gas counters can be employed to avoid this handicap, but for routine use they are difficult to operate and are time consuming.

Yankwich *et al.* (17) and Libby (7) discuss general methods for correction of self-absorption by samples of varying thicknesses of weak β -emitters. Hendricks *et al.* (3) give data on the self-weakening of S^{35} in barium sulphate. Henriques *et al.* (4) give an analytical procedure for S^{35} based on oxidation to sulphate ion by the Carius method and subsequent precipitation as benzidine sulphate. Unfortunately, the correction factors derived from this work are

* Less than 100 μ gm. per cm.²

† L. Yaffe and K. Justus at these laboratories have obtained some interesting information on backscattering of β -radiation which is to be published shortly in the *Canadian Journal of Research*.

‡ See L. E. Glandenin, *Nucleonics*, Jan. 1948, for further discussion of this point.

not based on the most recent values of the maximum energy of the S^{35} radiation, and cannot be readily applied to different counting arrangements.

In the work reported here, an "end-on" Geiger counter, having a 3.2 mgm. per cm^2 mica window, was used. The counter was mounted on a lucite

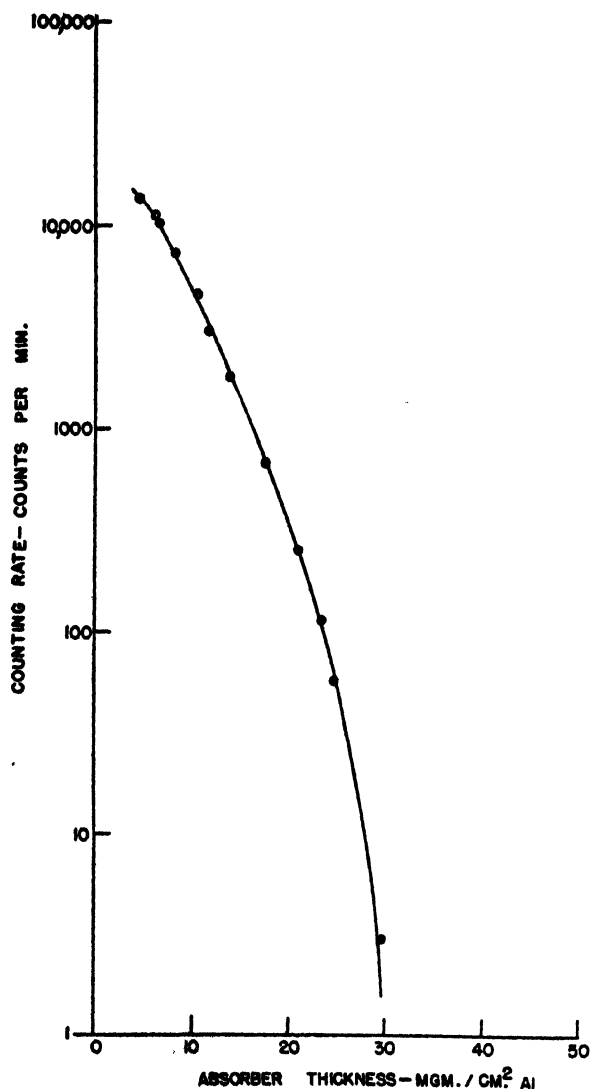


FIG. 1. Absorption measurements on S^{35} radiation (thin film mounting).

holder, and the air gap between counter and sample was held constant at 1.25 cm. Samples to be counted were deposited on watch glasses, 1 in. in diameter.

The self-weakening problem was handled as follows. All samples to be analyzed for S^{35} were made up to volume and aliquots of 0.1, 0.2, 0.3, 0.4 ml. were pipetted on to the watch glasses, evaporated to dryness, and counted.

The activities obtained were recalculated on a common volume basis, and the activity per unit volume plotted against the volume of the sample used. The curve was then extrapolated to zero volume (i.e., zero thickness of sample). It is evident that the curve must flatten as the volume approaches zero.

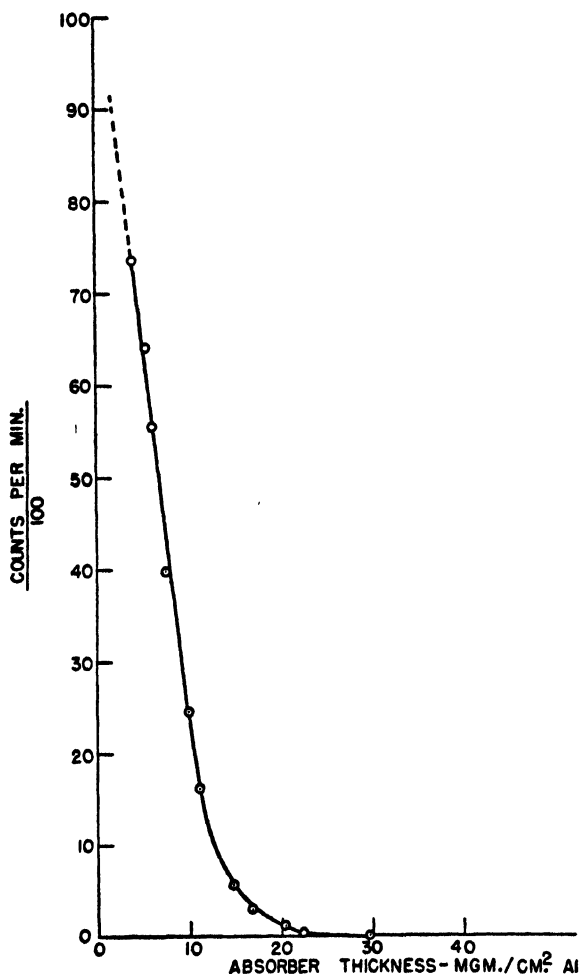


FIG. 2. Linear plot of external absorption (thin film mounting).

The activity reading at zero volume was taken as the "true" activity. This technique also served to minimize pipetting errors and check on possible evaporation losses.

EXTRACTION OF S^{35}

(a) Carbon Tetrachloride as the Target

Carbon tetrachloride was irradiated at very low neutron fluxes in an aluminum container. Considerable corrosion of the aluminum was found to occur over an irradiation period of one month.

In extracting the S^{35} , the procedure described by Kamen (5) was used as a guide. The irradiated carbon tetrachloride was refluxed with an aqueous

hydrogen peroxide solution containing some inactive sulphur and phosphorus carrier as ammonium sulphate and ammonium phosphate. The aqueous extract was separated, made basic, and magnesium ammonium phosphate precipitated. The filtrate was then made acid and barium chloride added to precipitate barium sulphate. Transfer of the precipitate was effected by slurring with ethyl alcohol. Activity yields obtained were of the order of $60 \pm 25\%$.

(b) *Potassium or Sodium Chloride as the Target*

Table II summarizes the relevant data as regards neutron irradiation of potassium and sodium.

TABLE II
REACTIONS OCCURRING ON NEUTRON IRRADIATION OF POTASSIUM AND SODIUM

Isotope	% abundance	Reaction	Product	Cross section, barns	Half life	Energy, Mev.		Remarks
						β	γ	
K ³⁹	93.38	n, γ	K ⁴⁰	?	1×10^9 yr.	1.0	2.0	K ⁴⁰ exists in nature
K ⁴¹	6.61	n, γ	K ⁴²	0.067	12.4 hr.	3.5	None	
Na ²³	100	n, γ	Na ²⁴	0.63	14.8 hr.	1.4	1.4	
						2.8		

The long half life of K⁴⁰ makes radioactivity from it negligible. The radiation from K⁴² and Na²⁴ would be troublesome unless a decay period of about one week is allowed. Storage and handling of irradiated sodium are somewhat more complicated than for potassium because of γ -ray emission from the former. The proportion of chlorine in potassium chloride is 47.56%, in sodium chloride is 60.7%.

(i) *Separation of S³⁵ from Irradiated Potassium or Sodium Chloride with Carrier*

A satisfactory procedure for separation of S³⁵ from the irradiated alkali chloride, using inactive carrier sulphur, involves the precipitation of barium sulphate.

The irradiated salt was dissolved in water and carrier ammonium sulphate and ammonium phosphate were added. Magnesium ammonium phosphate and barium sulphate were separated as described above.

Experiments were carried out to check on the following: (a) the need to oxidize the original solution, (b) coprecipitation of S³⁵ with magnesium ammonium phosphate when no carrier sulphate is added, and (c) coprecipitation of P³² with barium sulphate when no carrier phosphate is added.

Two equal aliquots of stock solutions of irradiated alkali chloride were treated as follows: carrier sulphate and phosphate were added, and one of the aliquots was oxidized with hydrogen peroxide, the excess peroxide being destroyed by heating in hot water. Both solutions were acidified with hydrochloric acid, barium sulphate precipitated from the hot solution, and

the precipitate digested for two to three hours. Table III gives the percentage of S^{35} activity left in the filtrate after precipitation. The activity due to P^{32} was eliminated by means of absorption measurements.

TABLE III
SEPARATION OF S^{35} USING CARRIER

Target material	Treatment	S^{35} left in filtrate, %
NaCl	Oxidized	0.5
NaCl	Nonoxidized	0.8
KCl	Oxidized	0.4
KCl	Nonoxidized	1.1

It will be seen that the percentage of S^{35} left in solution after precipitation of barium sulphate is slightly higher for the nonoxidized solutions. The actual values, however, are so small that it can safely be said that the chemical form of S^{35} in neutron irradiated potassium or sodium chloride is such that it will undergo rapid exchange with sulphate ion upon solution of the target material.

Voge and Libby (14) and Voge (13) found that exchange between sulphide and sulphate, and sulphite and sulphate, was not appreciable during 36 hr. at 100° C. It seems likely, therefore, that the radioactive sulphur appears as $S^{35}O_4^{2-}$ on water dissolution of irradiated potassium or sodium chlorides.

S^{35} does not coprecipitate appreciably with magnesium ammonium phosphate even if no carrier sulphate is added, if the solution and precipitate is digested in boiling water for a few hours. If barium sulphate is precipitated from hot acid solution, and digested for a few hours in boiling water, the contamination from P^{32} coprecipitation is negligible.

(ii) *Separation of S^{35} from Irradiated Potassium or Sodium Chloride Without Carrier*

In the extraction procedures described above, the S^{35} is considerably "diluted" with inactive sulphur. The limiting factors in the specific activity obtainable are: (a) the available neutron flux and (b) the quantity of carrier which must be added concomitant with the volume of solution needed to dissolve all the potassium or sodium chloride target material.

An increase in specific activity will be effected by the removal of the excess target material. Overman (9) mentions the use of ion-exchange resins for this purpose. Preliminary experiments performed by the writer using Dowex-50 as the ion-exchange resin were discouraging. Over 50% of the S^{35} was found to adsorb on the resin in a $\frac{1}{2}$ in. diameter column, 6 in. long. An alternative technique was therefore developed, based on the insolubility of potassium and sodium chlorides in concentrated hydrochloric acid.

Following preliminary beaker experiments to test the feasibility of the process, an apparatus (Fig. 3) was constructed which could be operated with

minimum direct handling of active materials. The apparatus is operated as follows. A stream of air is passed through the sintered glass disk (*B*) after having passed through a calcium chloride drying tube (*O*). The pressure

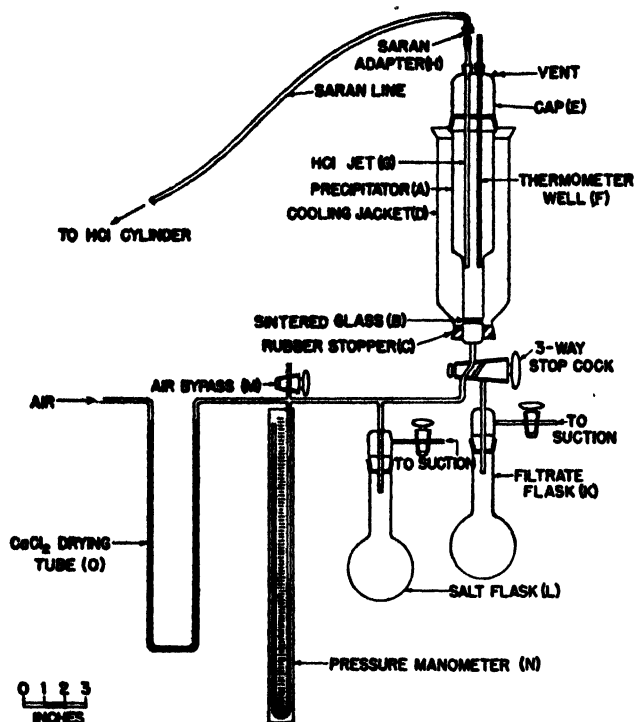


FIG. 3. S^{25} extraction apparatus.

manometer (*N*) is adjusted by control of a by-pass (*M*). A saturated solution (at room temperature) of the irradiated salt is poured into the precipitator (*A*), and is kept from running through the sintered glass by the air stream. The cap (*E*) is then put on, and hydrogen chloride gas (from a cylinder) is passed in through the jet (*G*). Cooling media (brine solution cooled by dry ice) is circulated through the cooling jacket (*D*). Since hydrogen chloride has a large heat of solution, the temperature can be used as a measure of the saturation of the solution. When the temperature of the solution falls to the desired value (-10 to -20°C.), the three-way stopcock (*J*) is turned and the filtrate drawn off by suction into a flask (*K*). The hydrogen chloride gas stream is then shut off, and the cap removed. Spray is washed from the sides of the vessel with a little concentrated hydrochloric acid.

This filtrate can then be evaporated to a small volume, concomitant with its reduced salt content, and the process repeated. The residual salt is dissolved in distilled water and drawn off after each precipitation (into flask *L*).

Two 25 gm. batches of irradiated potassium chloride (each dissolved in 100 ml. of water) were extracted in series. Their filtrates were evaporated together until a precipitate of potassium chloride appeared. Sufficient water for solution was added and a second extraction procedure carried out.

Similarly, 11 gm. of irradiated sodium chloride was put through a single precipitation procedure. Table IV lists the results obtained.

TABLE IV
SEPARATION OF S^{35} FROM IRRADIATED POTASSIUM AND SODIUM CHLORIDES

Target material	KCl	NaCl
Total weight of salt used, gm.	50	11
No. of precipitations	2	1
% Reduction in solids	99.8	99.8
% Yield of S^{35}		
In filtrate	85.5	81.0
In HCl washing	9.1	17.4
	94.6	98.4
% Lost in evaporation	1	—

The very high yields of S^{35} obtained by this process, from both potassium and sodium chlorides, together with the fact that a considerable quantity of activity is carried off by a very small volume of concentrated hydrochloric acid, would indicate that such losses as occur are due to simple wetting and not crystal occlusion. The difference in yield between sodium and potassium chlorides is not to be taken too seriously in view of the large difference in bulk of material extracted and the inaccuracies in counting S^{35} .

It is noteworthy that the solubility of sodium chloride in hydrochloric acid solutions is markedly lower than that of potassium chloride—one precipitation of sodium chloride yielding the same percentage reduction in solids as two potassium chloride precipitations.

As a possible adjunct to the procedure described above, some experiments were done on the precipitation of potassium chloride from a saturated hot solution, advantage being taken of the large temperature coefficient of solubility of potassium chloride in water. Irradiated potassium chloride was dissolved to saturation in distilled water at 70° C., cooled overnight to 10° C., filtered, and the precipitate washed with a small volume of water. It was found that about 25% of the activity remains in the precipitate. It is difficult to reconcile the different behavior, as regards contamination with S^{35} , of these two precipitation procedures.

The capacity of the apparatus shown is about 100 ml. as an upper and 5 ml. as a lower limit. If desired, the apparatus could be scaled up to accommodate much larger volumes. The lower volume limit for an apparatus of this type, below which spray losses would be excessive, is probably 1 ml.

Assuming an irradiation period of one S^{35} half life (87.1 days), a flux of 5×10^{12} neutrons per cm.² per sec., and cross section of 0.13 barn, the potential activity to solids ratio, assuming one precipitation step, would be 2 mc. per mgm. solids for potassium chloride and 3.5 mc. per mgm. solids for

sodium chloride. In fact, the effective cross section for the reaction is much larger than that used here, and hence the ratio of S^{35} to total solids would be much higher.

P^{32} formed by $Cl^{35} (n, \alpha) P^{32}$ remains with the S^{35} as a radioactive contaminant. The chemical form of the carrier-free S^{35} obtained by this process is presumably a solution of $Na_2S^{35}O_4$ or $K_2S^{35}O_4$ in hydrochloric acid. If the S^{35} is required in other chemical forms, it is likely that some inactive carrier would have to be added and normal chemical conversions carried out.

(c) Ferric Chloride as Target

Natural iron consists of Fe^{54} —6.04%, Fe^{56} —91.57%, Fe^{57} —2.11%, Fe^{58} —0.28%. On neutron irradiation, two reactions lead to radioactive isotopes: $Fe^{54} (n, \gamma) Fe^{55}$, $Fe^{58} (n, \gamma) Fe^{59}$. Fe^{55} decays by K capture, emitting a very soft X-ray, with a half life of about four years. Fe^{59} emits 0.26 and 0.46 Mev. β 's and 1.1 and 1.3 Mev. γ 's decaying with a 47 day half life. The total atom cross section for Fe^{59} formation is 0.001 barn.

It will be seen therefore that the interfering activity, in using ferric chloride as a target for making S^{35} , will be existent but slight. Ferric chloride consists of 34.45% iron and 65.55% chlorine.

(i) Separation of S^{35} from Irradiated Ferric Chloride with Carrier

Anhydrous, sublimed ferric chloride was irradiated with neutrons and a two day decay period allowed.* Experiments were carried out to determine (a) the chemical form of the S^{35} and (b) the coprecipitation of S^{35} with hydrated ferric oxide.

After solution of the irradiated ferric chloride, carrier sulphate and phosphate were added. Three aliquots were taken and to two of these a few drops of 30% hydrogen peroxide was added and the solutions heated to destroy excess peroxide. Barium sulphate was precipitated from both oxidized and unoxidized solutions, following the procedure described earlier.

Essentially no difference was found as a result of the oxidation step. The precipitation of barium sulphate leaves about 1% of the S^{35} in solution whether the solution is initially oxidized or not. It would appear, therefore, that on solution of irradiated ferric chloride, the S^{35} is present as $S^{35}O_4^-$, or in a form which exchanges rapidly with sulphate ion.

Hydrated ferric oxide was precipitated from the third aliquot by addition of concentrated ammonium hydroxide. About 50% of the S^{35} and practically 100% of the P^{32} is carried down in this precipitation. As a separation method, therefore, the precipitation of hydrated ferric oxide offers little advantage.

(ii) Separation of S^{35} from Irradiated Ferric Chloride Without Carrier

It is well known that ferric chloride can be readily solvent-extracted from aqueous hydrochloric acid solutions with diethyl or diisopropyl ether as well as other higher ethers. The real interest in using ferric chloride as a target

* Irradiation containers used were made of (a) aluminum and (b) bakelite. Both were satisfactory from a corrosion standpoint.

material lay in the likelihood of a very efficient and simple S^{35} extraction procedure based on the solvent extraction of ferric chloride.

In the experiments reported here, isopropyl ether was used as solvent. The partition coefficient for extraction of ferric chloride by isopropyl ether from aqueous 6 *M* hydrochloric acid varies from 1 to 100 (15), depending on the iron concentration. For higher acidities up to 8 *M* hydrochloric acid the coefficient is even higher.

One gram of pile-irradiated ferric chloride was dissolved in concentrated hydrochloric acid and a few drops of 30% hydrogen peroxide added, to ensure that all the iron was present as ferric ion. (Ferrous chloride does not solvent-extract.) The solution was then diluted with distilled water to approximately 6 *N* in hydrochloric acid.

The aqueous solution was shaken with successive $\frac{1}{4}$ volumes of isopropyl ether until the color of ferric chloride had disappeared completely. It was then extracted twice more with $\frac{1}{4}$ volumes, and finally washed with an equal

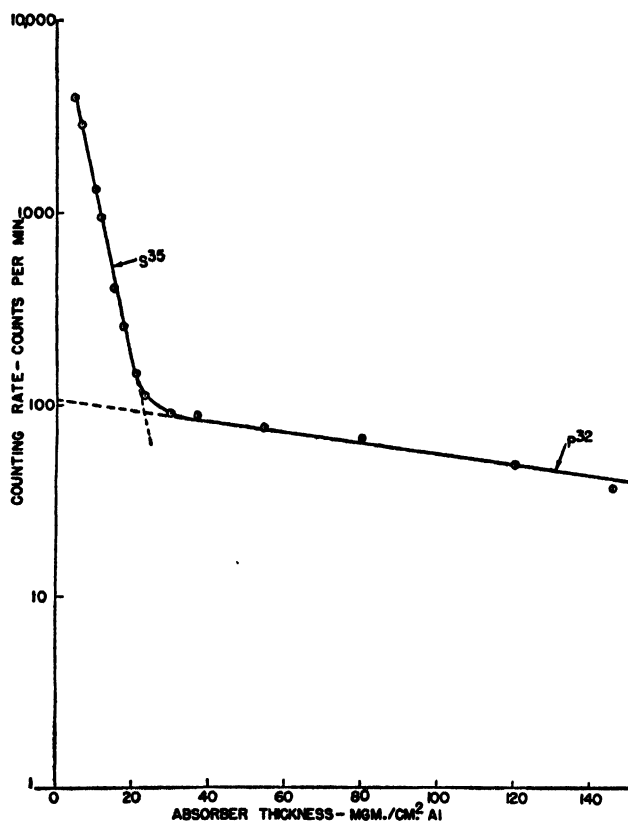


FIG. 4. Activity in aqueous residue solution.

volume of solvent. (The total volume of ether used depends on the initial concentration of ferric chloride and hydrochloric acid, as well as on the patience of the experimenter in shaking each batch for a sufficiently long period of time to ensure equilibrium.)

The ether extracts were then collectively stripped with distilled water.

The radioactivity of the resultant solutions was measured, components being differentiated by absorption measurements. An aliquot of the aqueous residue solution was evaporated to dryness to measure the total solids left.

Figs. 4, 5, and 6 give the absorption curves for the aqueous residue solution, the stripped ether, and the water extract respectively. It is evident that no detectable amount of radioactive iron remains in the aqueous residue. On the other hand, the radioactivity of S^{35} cannot be detected in the extract.

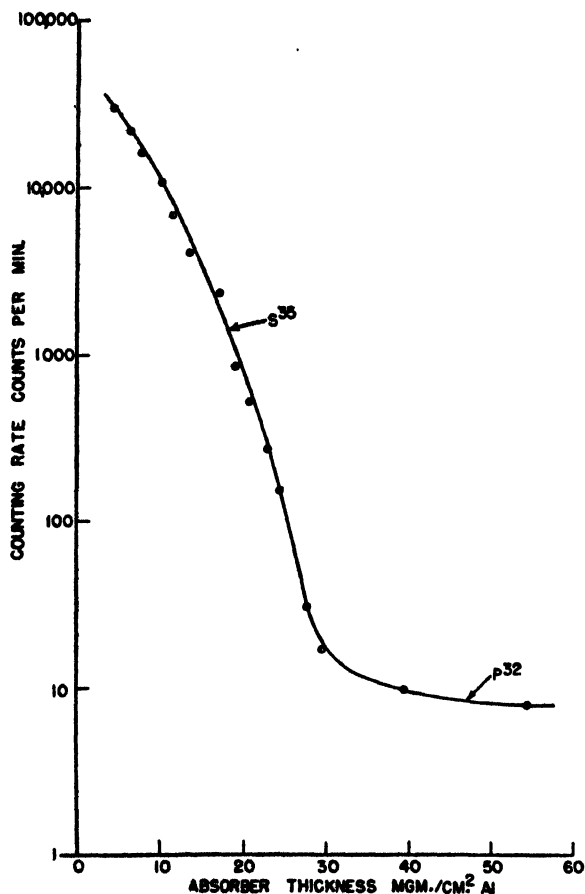


FIG. 5. Activity in stripped ether.

The sharpness of separation emphasizes the usefulness of the solvent extraction technique. It is of interest to note that the P^{32} is present in a form which is extractable to some extent—having a small but measurable partition coefficient. A small amount of S^{35} is taken up by the solvent and is not re-extracted by distilled water. Presumably this is S^{35} present as a sulphur chloride which is soluble in organic solvents.

A visible reddish residue remained on evaporation of the extracted solution, but its weight was less than the limits of sensitivity of the balance (10^{-4} gm.).

Table V summarizes the distribution of material and activity resulting from the above procedure.

TABLE V
SOLVENT EXTRACTION OF 1 GM. IRRADIATED FERRIC CHLORIDE

Solution	Solids content	S^{35} % of original	P^{32} % of original	Fe^{59} % of original
Aqueous residue	10^{-4} gm.	99.5	83	Undetectable
Stripped ether	10^{-3} gm.	0.5	0.01	"
Water extract	Bulk of original $FeCl_3$	Undetectable	17	100

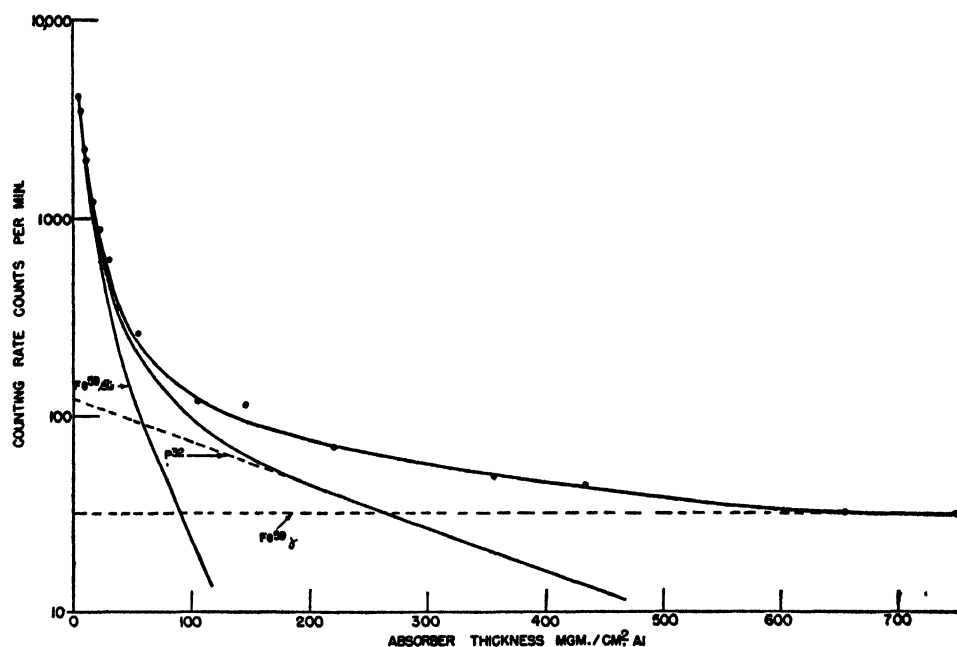


FIG. 6. Activity in water extract.

Assuming (a) 1 mgm. of solids remains per gram of original material, (b) a flux of 5×10^{12} neutrons per $cm.^2$ per sec., (c) the cross section for $Cl^{35}(n, p)S^{35}$ is 0.13 barn, (d) 87.1 days irradiation period, the potential activity concentration would be 100 mc. S^{35} per mgm. total solids—with no inactive sulphur carrier added. The chemical form of the S^{35} in the extracted solution is presumably as $FeS^{35}O_4$. P^{32} formed by side reaction remains as a radioactive contaminant.

Under the conditions outlined above, the Fe^{59} radioactivity would be approximately 80 $\mu c.$ per gm. ferric chloride. Thus, the ratio of $S^{35}:Fe^{59}$ would be about 1000 : 1, in the unextracted material.

For small amounts of ferric chloride (0.1 to 100 gm.) various types of apparatus could be employed to carry out the extraction with a minimum of handling. (1) The two phases could be contacted by a stirrer and the

solvent (top layer) removed by suction, in a series of batchwise extractions. (2) Solvent could be passed countercurrently through a static column of the aqueous solution overflowing at the top to a holding vessel. (3) A Soxhlet type of extractor could be employed, involving recirculation by distillation of a small volume of solvent.

Acknowledgment

Work on the problem of S^{35} preparation and extraction was started under the guidance of Dr. L. Siminovitch. The assistance of Dr. L. Yaffe in the editing of this paper is gratefully acknowledged.

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THE NITROLYSIS OF HEXAMETHYLENETETRAMINE

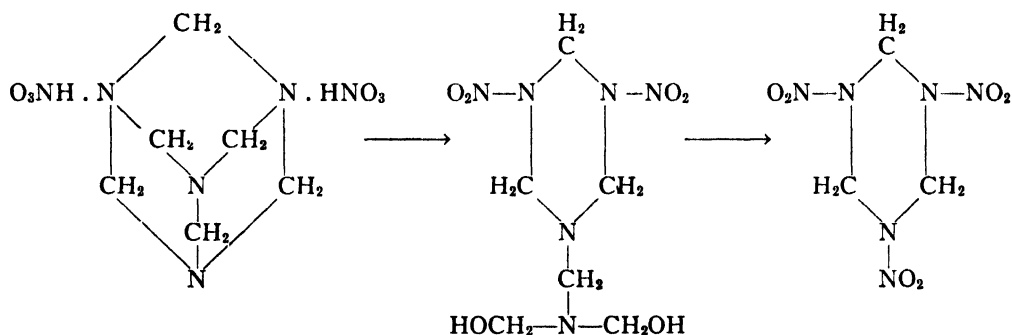
IV. SYNTHESIS OF A CYCLONITE HOMOLOGUE¹

BY G. S. MYERS² AND GEORGE F WRIGHT

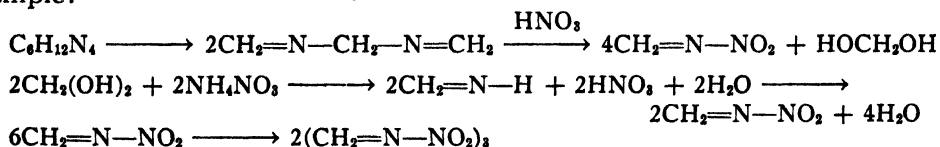
Abstract

A homologue of Cyclonite has been prepared. This homologue, 1,3,6-trinitro-1,3,6-triazacycloheptane was formed by nitrolysis of methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, which was synthesized from N,N'-dimethylol-1,2-dinitraminoethane, formaldehyde, and ammonia. The reliability of this synthesis was established by analogous reactions. The nitrolysis yields also 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane via 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane. Ammonium nitrate has been shown to promote demethylation in this series just as it does in the triazacyclohexane compounds. Analogies have therefore been drawn between these nitrolyses and that of hexamethylene-tetramine. Further comparisons derive from the isolation of 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane and 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane by acetolysis of methylene-bis-dinitrotriazacycloheptane with acetic anhydride.

The demonstration that nitrolysis of hexamethylenetetramine (hexamine) forms dimethylolnitramide (3) (or its nitrate ester) as well as Cyclonite has suggested a stepwise nitrolysis mechanism (4),



but one might also advance a fragment mechanism which involved disassembly of hexamine with subsequent reassembly to Cyclonite, for example:



Since the hexamine molecule consists entirely of alternate C—N—C linkages it is difficult to decide between these two mechanisms. Either is logically reasonable on the basis of the symmetrical products containing the C—N—C linkage, which are formed. However if the final product lacked the symmetry of Cyclonite, the probability of reassembly of nitrated fragments to

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give a single cyclic product would be exceedingly remote. We have prepared a homologue of Cyclonite (1,3,5-trinitro-1,3,5-triazacycloheptane) which lacks this symmetry and find that it is not contaminated with Cyclonite. This would suggest, by analogy, that Cyclonite itself is formed by stepwise degradation of hexamine.

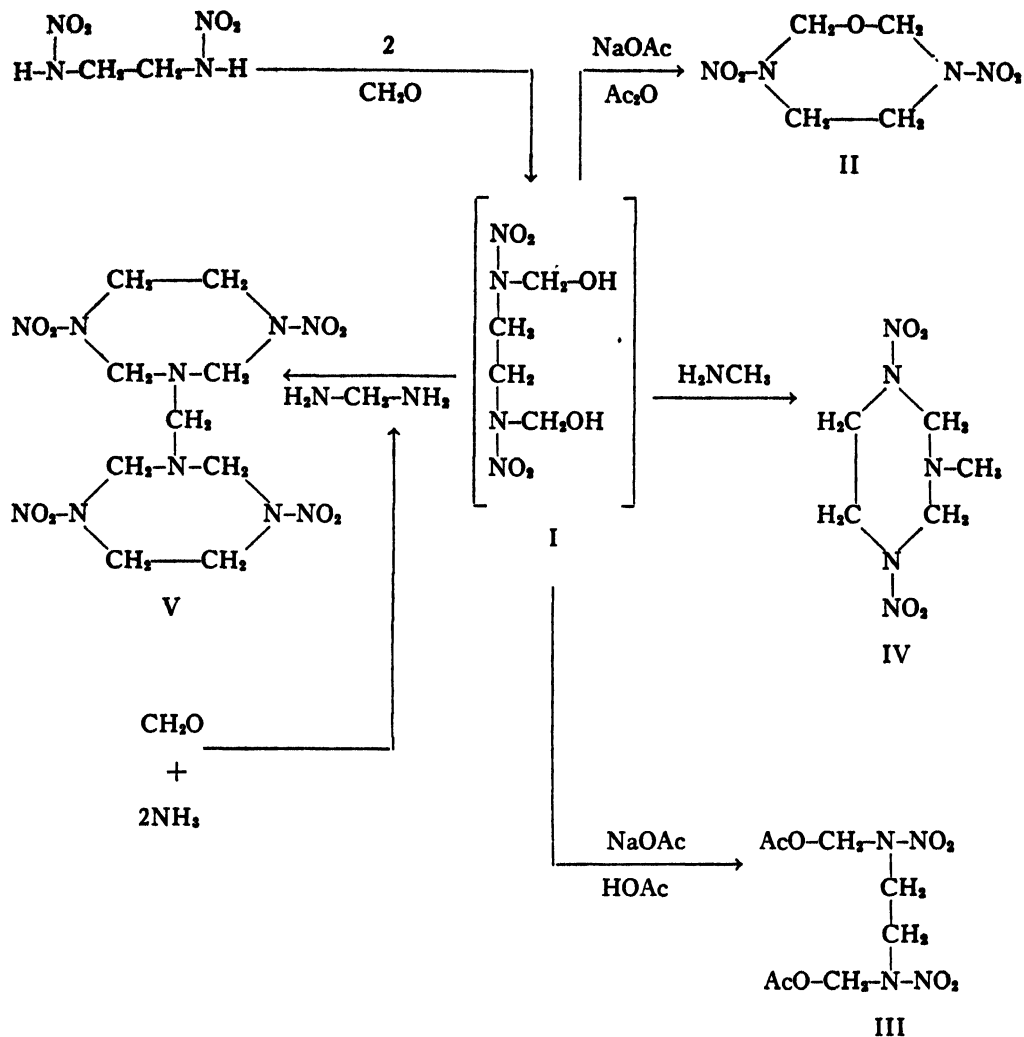
The preparation of compounds containing the triazacycloheptane ring required homologues of the substances synthesized earlier (3) from nitramide formaldehyde, and various amines. This was accomplished simply by utilizing 1,2-dinitraminoethane instead of nitramide. A description of these homologues and their characteristic reaction products forms the basis of the present report.

Since ethylenedinitramine is relatively insoluble in water, the slow solubilization by addition of two equivalents of formaldehyde is strongly indicative of the formation of N,N'-dimethylol-1,2-dinitraminoethane, I, even though this compound cannot be isolated. N-monomethylol-1,2-dinitraminoethane is always obtained instead (1, 7). The diacetate ester, however, can be prepared by treating the aqueous formaldehyde-ethylenedinitramine solution with sodium acetate and just sufficient acetic anhydride to convert the water to acetic acid. A 63% yield of N,N'-diacetoxymethyl-1,2-dinitraminoethane, III, was obtained by heating this solution to 65° C. The same compound can be obtained in 53% yield from N-monomethylol-1,2-dinitraminoethane without additional formaldehyde, so that ethylenedinitramine and its two methylol derivatives must represent an equilibrium system involving formaldehyde. This behavior is characteristic also of the formaldehyde-nitramide-dimethylolnitramide system (3).

The formation of the acetate ester, III, was carried out in the acetic acid produced by aqueous hydrolysis of acetic anhydride. If sufficient anhydride is used so that some remains after this water is consumed, the product which has been reported is 1,5-dinitro-3-oxa-1,5-diazacycloheptane, II (7).

There seems, then, to be little doubt that dimethylolethylenedinitramine exists in water solution, and therefore should undergo the same type of condensation observed with dimethylolnitramide (3). Reactions of this type have been observed. When the aqueous solution of I is treated with methylamine a compound precipitates which is 3,6-dinitro-1-methyl-1,3,6-triazacycloheptane, IV, on the basis of analyses, both elemental and functional for methylamine and formaldehyde. Although the compound is not very stable, a hydrochloride can be prepared which accounts for the one basic amino group in the structure.

If, instead of methylamine, a solution of formaldehyde and ammonia is treated with a solution of I, a compound is precipitated which we have specified as methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V, on the basis of elemental analysis and functional analyses for ammonia, formaldehyde (5), and ethylenedinitramine. The compound largely decomposes in dilute hydrochloric acid, although a small amount can be recovered by neutralization. No salt could be prepared.

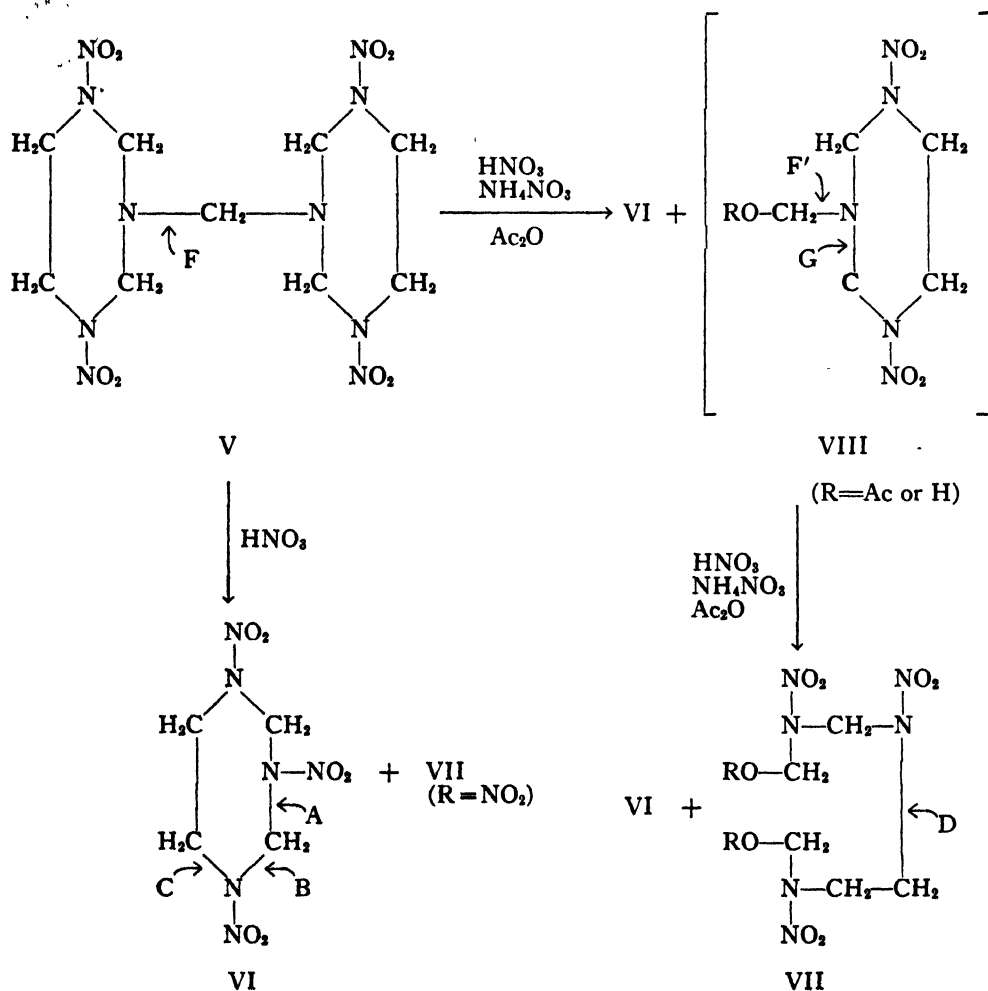


These condensations, as well as those reported previously (3), may be seen to be of the Mannich type, and in this connection it is significant to note that in all such reactions with nitramides, the condensation seems to take place between the nitramide-formaldehyde addition product and the amine, rather than with the free nitramide and the amine formaldehyde addition product.

The formation of many-membered rings seems quite common among these condensations, and no restriction favoring five- and six-membered rings seems to apply when nitrogen is included in the cycle. Indeed the ease with which seven- and eight-membered rings will form in these condensations would seem not to exclude larger cycles, so that one might consider 1,8-*endomethylene*-3,6,10,13-tetranitro-1,3,6,8,10,13-hexaazacyclotetradecane as reasonable a structure for V as the *bis*-triazacycloheptane which has been diagrammed. Either could have formed from the methylenediamine which we consider to be the reaction species in formaldehyde-ammonia (3, 6).

The nitration of V does, however, recommend the triazacycloheptane structure. When methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane, V, is treated at 0° C. with 20 moles of 99% nitric acid and then diluted and neutralized, an impure precipitate is obtained which is probably contaminated with 1,8-dinitroxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R=NO₂), although we were not able to identify this compound. The isolable product in its crude form was obtained in 76% yield (1 mole V→1 mole VI) if it is 1,3,6-trinitro-1,3,6-triazacycloheptane, VI. Its elemental analysis conforms with this structure.

This Cyclonite homologue, VI, resembles Cyclonite in its solubility in organic solvents, but it is much less stable and, indeed, is destroyed slowly by boiling water (7% in two hours). The marked difference in stability in contrast to



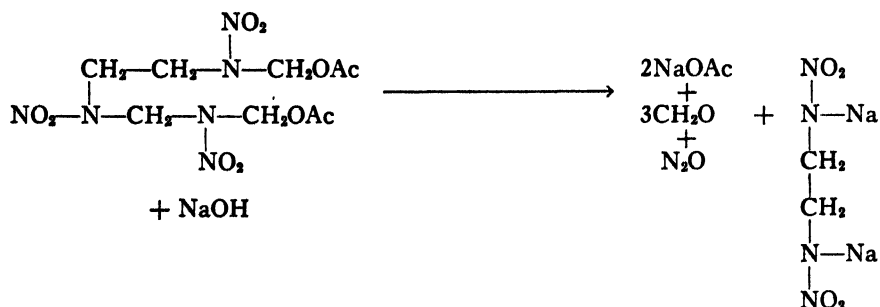
Cyclonite (RDX) or 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane (HMX) finds an explanation when 1,3,6-trinitro-1,3,6-triazacycloheptane, VI, is hydrolyzed by 5% aqueous sodium hydroxide. Decomposition is complete in 10 min. and *no* ethylenedinitramine can be isolated. A control

experiment shows that 97% of ethylenedinitramine itself can be recovered from such alkaline treatment. This must mean that scission of VI occurs at C rather than at A or B. One may infer from this behavior that the methylenedinitramine linkage $\text{—NO}_2\text{N—CH}_2\text{—NNO}_2\text{—}$ is much stronger than homologous alkylenedinitramines. In the event that the ends of a polymeric methylenenitrimine chain ($\text{—CH}_2\text{—[N}_2\text{O}_2\text{—CH}_2\text{]}_n\text{—N}_2\text{O}_2\text{—}$) are blocked with methylenenitramine linkages of like strength, then terminal attack is likewise minimized. This is the situation in the two most stable nitramines, RDX and HMX, which are cyclic; it suggests resonance hybridization.

The preparation of trinitrotriazacycloheptane is somewhat more definitive when methylene-*bis*-dinitrotriazacycloheptane, V, is treated with the reagents used by Bachmann for Cyclonite preparation (2). One mole of V is suspended in 10 moles of acetic anhydride and stirred at 50° to 60° C. while a solution of ammonium nitrate in nitric acid is added over three minutes. The gum which separates after neutralization of the water-diluted mixture can be solvent-separated into a 47% yield of trinitrotriazacycloheptane (1 mole V \rightarrow 1 mole VI) and a second compound, in 43% yield if it were 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R = Ac). The structure of VII was based on elemental and acetyl analyses.

Although no analyzable derivative of 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, has been obtained, the compound yields, with 98% nitric acid at 0° to 5° C., a product which is evidently VII (R = NO₂). This product is so unstable that it decomposes after a few minutes at room temperature. This instability precludes its possible conversion to the dimethoxy derivative, (VII) (R = CH₃), since this reaction involves warm methanol. The crude material was, however, reconverted in 40% yield to VII (R = Ac) by treatment with sodium acetate in acetic acid at room temperature. This excludes an alternative structure for VII (R = Ac) such as 9-acetoxy-8-nitroxymethyl-3,6-dinitro-3,6,8-triazanonanone-2, because nitration followed by acetylation would not have regenerated the original compound.

The alkaline hydrolysis of 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, yields only 82% of the ethylenedinitramine expected from the equation



This would indicate that the terminal acetoxy groups have prevented degradation from the ends of the alkylenedinitramine structure to an extent somewhere

between that in VI, where total destruction of the ethylenedinitramine occurred, and that in V where none of the constituent ethylenedinitramine is destroyed. This indication is, of course, based on the assumption that if degradation cannot occur *toward* the integral ethylenedinitramine linkage (that is, from the ends of a chain of atoms) then scission will occur such as is illustrated at D in VII.

Thus far in this report the scission products of methylene-*bis*-dinitrotriazacycloheptane, V, have resulted from media involving nitric acid. However acetic anhydride alone splits the compound, although somewhat more slowly than does nitric acid. A six hour period of boiling with the anhydride in acetic acid produces the expected two compounds. The less soluble 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane (VIII, R=Ac) precipitates from the cold reaction mixture. The lesser yield of 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane may be attributed to its greater solubility in the acetic acid medium where impurities prevent its separation.

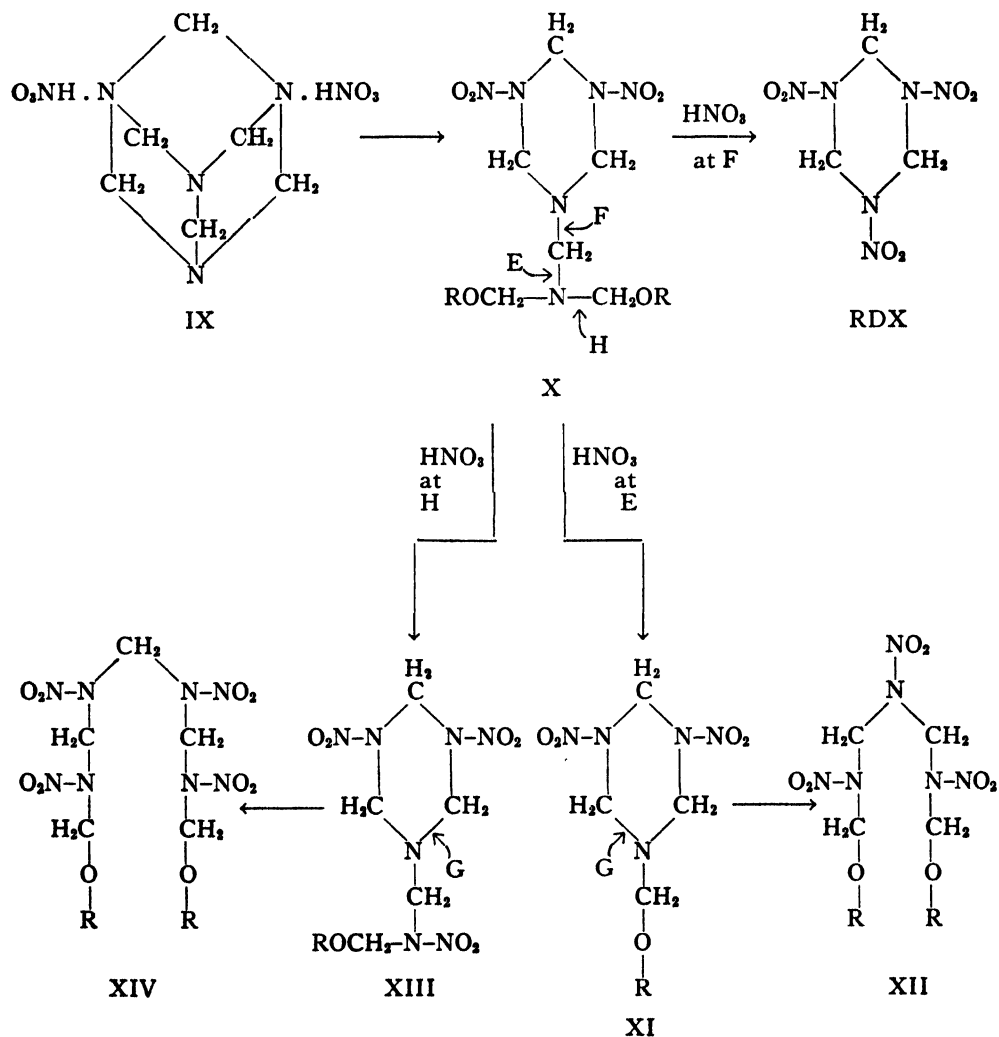
The acetoxymethyl group in acetoxymethyl dinitrotriazacycloheptane (VIII, R=Ac) is extremely labile and is converted either to the analogous propyl ethers (VIII, R=C₃H₇) or the ethyl ether (VIII, R=C₂H₅) by crystallization from the requisite alcohol. The ethoxymethyl compound can be converted by treatment with 99% nitric acid to trinitrotriazacycloheptane, VI, in small (6%) yield. Because of the lability of the pendulous group one might expect replacement of the acetoxymethyl group by nitro, via demethylolation, at F' (structure VIII) upon treatment with the Bachmann reagents, acetic anhydride, ammonium nitrate, and nitric acid. Indeed this occurs at 60° C., but trinitrotriazacycloheptane is not the only product. Scission of the ring also occurs at G as shown in structure VIII to give 1,8-diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII (R=Ac). According to the relative amounts of product which were obtained, 73% of the scission occurs at F' and 27% at G.

It is probably unsafe to evaluate the relative strengths of the linkages in V and VIII (R=Ac) on the basis of the 52 : 48 ratio versus the 73 : 27 ratio of trinitrotriazacycloheptane VI to diacetoxytrinitrotriazaoctane, VII, obtained respectively from the two compounds. Firstly there is no assurance that R is not partly NO₂ when VIII is a transient intermediate in the conversion of V to VI and VII. Secondly the lesser total yields obtained from methylene-*bis*-dinitrotriazacycloheptane, V, would indicate a high ammonium nitrate consumption by the formaldehyde freed because of side reactions. If ammonium nitrate is actually the reagent responsible for demethylolation, then demethylolation to produce trinitrotriazacycloheptane would be decreased in nitrolysis of V as compared with nitrolysis of VIII because relatively less of the reagent would be available over the reaction life of V than it would be during the more efficient nitrolysis of VIII.

The latter assumption that ammonium nitrate is the demethylolation agent seems quite reasonable in view of the fact that acetoxymethyl dinitrotriazacycloheptane, VIII, yields no isolable amount of trinitrotriazacycloheptane, VI, when it is treated with acetic anhydride and nitric acid in absence of

ammonium nitrate. Under these conditions scission seems to take place principally at G to give an 82% yield of diacetoxytrinitrotriazaoctane, VII.

On the basis of these data, and the compounds which have been isolated, the mechanism of nitration of methylene-*bis*-dinitrotriazacycloheptane, V, seems to be first a scission at F to produce VI and the transient fragment VIII. The fate of this fragment will depend on the available amount of ammonium nitrate to demethylolate it at F' in order to form more trinitrotriazacycloheptane, VI, since otherwise scission will occur at G to give VII (R = Ac.). No other structures are possible except one which places two nitro groups on one nitrogen (such structures are unknown) or one in which a reversed fission has produced a nitroso-acetamide compound. The latter behavior is unknown, but it would still involve fission at G. The final alternative, 9-acetoxy-8-nitroxymethyl-3,6-dinitro-3,6,8-triazanonanone-2 would not be expected to give the precise acetyl values which were obtained for VII (R = Ac) nor could it have been nitrated and then reacylated to be regenerated in its original form.



In so far as analogies between triazacyclohexane and triazacycloheptane rings are valid, one can assume that when hexamine dinitrate, IX, nitrolyzes to form the primary scission product, X, the subsequent scission is probably largely at F with lesser amounts at E and H to account for the limited amounts of by-products such as XII via XI, and XIV via XIII when esterification occurs at E or H. While such a concept does not preclude a stepwise demethylation (down to linkage F) of nonesterified X, it excludes XI as a significant intermediate in the formation of RDX. This follows by analogy with the triazacycloheptane chemistry reported here, since XI might be expected to split appreciably at position G. This exclusion of XI as intermediate applies only to the reaction where demethylation can proceed normally. When esterification is promoted strongly and demethylation is correspondingly retarded, the scissions at H and especially at E may become preponderant.

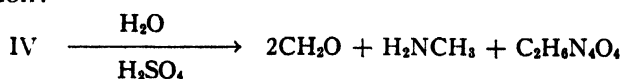
Experimental*

3,6-Dinitro-1-methyl-1,3,6-triazacycloheptane, IV

Finely ground ethylenedinitramine, weight 9.0 gm. (0.06 mole) was suspended in 18.4 cc. (0.24 mole) of 37% formalin. The slurry was warmed to 60° C. and stirred for 11 min. until solution was complete. After five minutes longer at 60° C., the solution was cooled to 0° C. No insoluble material appeared at this stage. A 30% aqueous methylamine solution, 12.4 cc. (0.12 mole), was added dropwise with cooling to the reaction mixture over a three minute period. The white crystalline precipitate which formed almost at once was further agitated for 20 min. at 0° C. and then filtered off. The product, washed with 300 cc. water and dried at 50° C., weighed 10.23 gm. (83% theory, ethylenedinitramine basis) and melted at 158° to 160° C. with frothing.

Dinitromethyltriazacycloheptane is insoluble in water, dilute alkali, cold ethanol, and ether but is soluble in hot benzene, acetic acid, and ethyl acetate and in cold acetone, methyl ethyl ketone, and nitromethane. It is fairly stable in warm solvents and is purified easily from hot ethyl acetate from which it separates on cooling in needlelike crystals, m.p. 159° C. Calc. for $C_6H_{11}N_6O_4$: C, 29.2; H, 5.42; N, 34.1%. Found: C, 29.5; H, 5.44; N, 34.0%.

Formaldehyde and methylamine analysis, carried out according to the method of Meyer (5) were both higher than would be expected from the following equation:



However, when ethylene dinitramine was carried through the same analytical procedure it indicated a content of 17.1% formaldehyde and 3.0% ammonia. The formaldehyde analysis on IV was found to be 43.6%; the methylamine

* All melting points have been corrected against reliable standards.

was 20.2%. If the ammonia and formaldehyde values for the ethylenedinitramine content of IV are subtracted, then percentages are obtained which are in fair agreement with the calculated value. Calc. for $C_5H_{11}N_5O_4$: $2CH_2O$, 29.3; CH_3NH_2 , 15.1%. Found: $2CH_2O$, 31.1; CH_3NH_2 , 16.1%.

We were unable to prepare a picrate of dinitromethyltriazacycloheptane but the hydrochloride was prepared by addition of dry hydrogen chloride to a solution of 0.30 gm. (0.00147 mole) of IV in 30 cc. benzene until precipitation was complete. The salt was filtered, benzene washed, and dried at 50° C. It weighed 0.29 gm. (80% of theoretical) and melted at 138° to 140° C. with violent frothing. An otherwise similar preparation in acetone gave a yield of only 8%, and the decomposition product, ethylenedinitramine, was found in large quantity in the solution. Calc. for $C_5H_{12}N_5O_4Cl$: C, 24.9; H, 5.01; N, 29.0%. Found: C, 25.4; H, 4.86; N, 28.5%.

Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V

A suspension of 138 g. (0.90 mole) of ethylenedinitramine in 275 cc. (3.60 mole) of 37% formalin was warmed to 60° C. with stirring. The ethylenedinitramine went into solution in five minutes. After 15 min. longer at 60° C., it was cooled to 20° C., then 245 cc. (3.60 moles) of 28% ammonia was added over a 20 min. period. The temperature was maintained at 20° to 40° C. with an ice bath. The sticky viscous solid which separated was difficult to stir, but when ground in a mortar, it solidified to a white amorphous solid which subsequently was stirred with 1500 cc. of water at 25° C. for one hour. After filtration and drying at 50° C., it weighed 110 gm. (63% on ethylenedinitramine basis) and melted at 197° to 198° C. (soft 196° C.). When the initial formaldehyde addition was increased to 7.2 moles the yield was raised to 94%.

The compound is insoluble in hot ethyl acetate, ethanol, benzene, acetic acid, and 10% sodium hydroxide. It is soluble in warm acetone and ethyl methyl ketone and also in cold concentrated and dilute hydrochloric acid. It can be purified by solution in warm acetone and precipitation with petroleum ether (b.p. 60° to 70° C.) to yield small white crystals, m.p. 205° C. (brown, decomp.). Calc. for $C_9H_{18}N_{10}O_8$: C, 27.5; H, 4.59; N, 35.0%. Found: C, 27.6; H, 4.59; N, 35.0%. The formaldehyde and ammonia analyses were CH_2O , 53.1%, and NH_3 , 13.3%. When these were corrected for the blank with pure ethylenediamine they became CH_2O , 40.1%; NH_3 , 11.0%. The calculated values (1 mole V gives $5CH_2O$ and $2NH_3$) are: CH_2O , 38%; NH_3 , 8.6%. The deviations are undoubtedly owing to the erratic hydrolysis of ethylenedinitramine in dilute sulphuric acid.

1,3,6-Trinitro-1,3,6-triazacycloheptane, VI

To 25 cc. (0.60 mole) of 99% nitric acid which was cooled to 2° C. in a three-necked flask was added, with stirring, 10 gm. (0.026 mole) of finely ground methylene-bis-dinitrotriazacycloheptane, V, over a 15 min. period. The reaction temperature which was held at 2° to 4° C. with an ice-salt bath during the addition, was maintained at 0° C. during the subsequent stirring period of 90 min. The content of the flask was then drowned in 500 cc. of ice and water

and this slurry was neutralized to pH 6 with 28% ammonia. Although 1.57 gm. of the precipitate was a solid, m.p. 134° to 138° C., the greater part was a gum which was converted to 3.10 gm. of powder, m.p. 152° to 153° C. (soft 150° C.) by stirring for five hours at 25° C. with 25 cc. of 95% ethanol. The total weight of crude (4.67 gm.) might be considered as a 38% yield if 1 mole of methylene-*bis*-dinitrotriazacycloheptane were nitrated to 2 moles of trinitrotriazacycloheptane.

A second preparation was carried out identically except that 40 equivalents (instead of 20 equivalents as above) of nitric acid were used per mole of slightly impure V (m.p. 198° to 199° C.). It was found that the gummy crude material could be purified equally well by washing with acetone or cooking with methanol. The total yield of trinitrotriazacycloheptane was 9.77 gm., m.p. 161° to 163° C. or 16.5% on the 1 mole to 2 mole basis. No other product could be discovered in the purifying solutions.

Trinitrotriazacycloheptane is insoluble in warm ethanol, benzene, acetic acid, chloroform, and ether but is very soluble in acetone, methyl ethyl ketone, nitromethane, and dioxane. The compound is decomposed by boiling in water, but can be crystallized by solution in hot acetone to which is then added petroleum ether (b.p. 60° to 70° C.). Two polymorphs are obtained, one (α) is a heavy prismatic crystal, the other (β) short and acicular. Both melt at 165° to 165.5° C. with decomposition, when they are separated mechanically. Calc. for $C_4H_8N_6O_6$: C, 20.4; H, 3.44; N, 35.6%. Found: C, 20.4; H, 3.41; N, 35.6%.

1,8-Diacetoxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, (R=Ac)

A suspension of 2.0 gm. (0.005 mole) of finely ground methylene-*bis*-dinitrotriazacycloheptane, V, in 5.1 cc. (0.051 mole) of acetic anhydride was stirred, initially at 60° C. while a solution of 0.48 gm. (0.0060) mole of ammonium nitrate in 0.51 cc. (0.012 mole) of 99% nitric acid was added over a three minute period. A cooling bath maintained the reaction between 60° and 70° C. After 20 min. subsequently at 60° C. the whole was drowned in 150 cc. of ice-water mixture. The slurry was immediately neutralized to pH 6 by addition of 28% ammonia; the sticky mass of solid which settled out was filtered off and suspended in ethanol for 12 hr. This ethanol treatment converted the gum to a granular precipitate which was filtered off, washed with ether, and dried at 50° C. It weighed 1.83 gm. and melted at 115° to 130° C. (soft 105° C.). This crude product was separated by solution in warm acetone and precipitation into petroleum ether (b.p. 60° to 70° C.) to give trinitrotriazacycloheptane VI, m.p. 162° to 163° C. (47% yield, 1 : 1 basis, estimated from these crystallizations), and a second compound melting at 97° to 98° C. after repeated acetone-petroleum ether crystallizations 56 \rightarrow 20° C. Estimated yield was 43% on the 1 : 1 basis. This second compound seems, according to its analyses, to be diacetoxytrinitrotriazaoctane, VII, (R=Ac). Calc. for $C_9H_{16}N_6O_{10}$: C, 29.4; H, 4.37; N, 22.8; CH_3CO , 23.4%. Found: C, 29.5; H, 4.35; N, 22.7; CH_3CO , 22.8%.

1,8-Dinitroxy-2,4,7-trinitro-2,4,7-triazaöctane, VII, (R = NO₂).

To 7 cc. (0.016 mole) of 98% nitric acid at 0° C. was added with shaking 1 gm. (0.00272 mole) of VII (m.p. 97° to 98° C.) over four minutes. The resulting solution was kept at 0° C. for seven minutes longer and then drowned in 10 parts ice-water mixture. A fluffy white solid separated out. A melting point could not be taken since this product became sticky on removal from the medium. It could not be purified from dioxane, carbon tetrachloride, or acetone. The absence of any unnitrated VII in this product was demonstrated by allowing the crude material to stand at 5° C. in 10 cc. of water to which a few drops of ammonia had been added. After two days at this temperature the material had decomposed and no water insoluble material remained. A test portion of VII (R = Ac) survived this treatment, so none of the acetate ester was present in the damp product.

The damp product obtained by this ester-interchange of VII with nitric acid was suspended in a solution of 1 gm. sodium acetate in 10 cc. acetic acid and 4 cc. acetic anhydride at 25° C. It dissolved completely in 15 min. The resulting solution was allowed to stand for 20 hr. and then drowned in water. The gummy suspension was extracted with 40 cc. ethyl acetate, the extract washed twice with water and concentrated to dryness *in vacuo*. The residue was dissolved in 5 cc. acetone-methanol and the solvent allowed to evaporate slowly over four days. The crystal crop weighed 0.40 gm. and melted at 82° to 87° C. This crude 40% yield was crystallized from acetone-ethanol to melt at 96° to 97° C. A mixed melting point with VII (R = Ac) was not lowered.

Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane with Acetic Anhydride

A suspension of 0.2 mole (78.8 gm.) crude methylene-bis-dinitrotriazacycloheptane (m.p. 185° C.) in 0.4 mole (40 cc.) of acetic anhydride and 400 cc. of glacial acetic acid was boiled under reflux for eight hours and then filtered to remove insoluble material. From the cooled filtrate there precipitated 32.4 gm. of material melting at 183° to 184° C. This was crystallized from 350 cc. of boiling acetic acid to yield 29.1 gm., m.p. 182.7° to 183.7° C. Recrystallization (15 cc. per gm.) from the same solvent did not raise this melting point. Yield of the crude 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane (VIII, R = Ac) is 55% of theoretical (1 : 1 molar basis). Calc. for C₇H₁₃N₅O₆ : C, 31.9; H, 4.98; N, 26.6%. Found: C, 32.2; H, 5.05; N, 26.5%.

The filtrate from which crude VIII was removed was diluted with 750 cc. of ether. After two days this was filtered to remove a gummy solid melting roughly at 144° C., which was dissolved in 25 cc. of hot nitromethane. On cooling, 4.23 gm. precipitated, m.p. 153° to 153.5° C. Dilution of the filtrate with 30 cc. ether yielded 3.20 gm. more, melting above 150° C. The total crude yield was 16% of theoretical. This 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane was purified in 58% recovery from boiling nitromethane (1.6 cc. per gm.) to melt at 153.8° to 154.2° C. No water insoluble product was isolated after this compound was dissolved in 95% nitric acid for one hour. Calc. for C₈H₁₁N₅O₆ : C, 30.9; H, 4.76; N, 30.1%. Found: C, 31.1; H, 4.80; N, 30.3.

1-Ethoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane

When 0.019 mole (4.98 gm.) of 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane was dissolved in 205 cc. of boiling absolute ethanol over 10 min. the filtered solution when cooled yielded 3.32 gm. of needles melting at 165.8° to 166.4° C. or 70% of theoretical. Crystallization from 13 cc. ethanol plus 18 cc. acetic acid gave a 75% recovery of material melting at 166.2° to 166.4° C. This melting point was not raised by recrystallization from boiling absolute ethanol (37 cc. per gm.) to give a 79% recovery. Calc. for $C_7H_{15}N_5O_5$: C, 33.7; H, 6.06; N, 28.2%. Found: C, 33.8; H, 6.04; N, 28.1%.

The reaction is more conveniently carried out if 20 cc. each of absolute ethanol and glacial acetic acid are used instead of the 205 cc. of ethanol alone. The yield is slightly higher (78%) than when ethanol alone is used.

A 0.27 gm. sample of the ethoxymethyl compound after boiling with 4 cc. of 5% aqueous sodium hydroxide for eight minutes yielded, after acidification with hydrochloric acid to pH 1, 0.17 gm. or 63% of its weight of ethylene-dinitramine (theory requires 60.3%).

When 1.25 gm. (0.005 mole) of this ethoxymethyldinitrotriazacycloheptane was added to 4.6 cc. (0.055 mole) of 99% nitric acid at -45° C. it dissolved completely. After warming to 25° C. over five minutes, it was poured into ice and neutralized with ammonia. The precipitate weighed 0.15 gm. and melted at 110° to 164° C. This was dissolved in 3 cc. hot acetone and cooled to precipitate a compound, not yet identified, which was filtered off and melted at 189.5° to 190.5° C. The filtrate was fractionally precipitated by addition of petroleum ether (b.p. 60° to 70° C.) to yield 0.07 gm. which melted from 140° to 162° C. This was crude trinitrotriazacycloheptane, VI, (6% yield), which was identified, after purification from 1 : 1 acetone - petroleum ether, by melting point (165.5° C.) and mixed melting point with an authentic sample.

1-Propoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane

The normal propyl ether (m.p. 136.8° to 138.2° C.) or the isopropyl ether (m.p. 182.2° to 184.6° C.) were formed more easily than the ethyl ether by repeated crystallizations of acetoxymethyldinitrotriazacycloheptane from the appropriate alcohol. Calc. for $C_8H_7N_5O_5$: C, 36.5; H, 6.49; N, 26.6%. Found for normal ether: C, 36.2; H, 6.32; N, 26.6%. Found for iso ether: C, 36.8; H, 6.49; N, 26.2%.

Nitrolysis of 1-Acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane, VIII

A. With acetic anhydride - nitric acid.—A suspension of 2.63 gm. (0.01 mole) acetoxymethyldinitrotriazacycloheptane in 10.4 cc. (0.102 mole) of acetic anhydride and 0.46 cc. (0.011 mole) of 99% nitric acid was stirred for four hours at 25° C., then 30 min. at 50° C. The reaction mixture, poured into ice and neutralized with 25 cc. of aqueous ammonia, yielded 2.97 gm. (82% of theoretical) of diacetoxyltrinitrotriazaoctane, VII ($R = Ac$), melting at 91° C., with prior softening. Solution of this crude product in 7 cc. acetone

yielded on dilution with petroleum ether (b.p. 60° to 70° C.) 2.22 gm. in three successive crops melting at 98° C., 97.5° C., and 96.5° C. None of the trinitrotriazacycloheptane could be discovered.

B. With acetic anhydride – nitric acid – ammonium nitrate.—A slurry of 9.96 gm. (0.038 mole) of acetoxymethyl dinitrotriazacycloheptane in 20.8 cc. (0.204 mole) of acetic anhydride was stirred at 60° C. while 1.92 gm. (0.024 mole) of ammonium nitrate in 2.04 cc. (0.048 mole) of 99% nitric acid was added over 15 min. After 20 min. subsequent stirring the whole was poured into ice and neutralized with 38 cc. of aqueous ammonia. The solidified gum, after two hours, was filtered; it weighed 11.7 gm. and melted below 90° C. This was dissolved in acetone and fractionally precipitated with petroleum ether (b.p. 60° to 70° C.) to yield first trinitrotriazacycloheptane and then diacetoxyl trinitrotriazaoctane in approximately equal amounts. These amounts correspond to yields of 65% and 25% respectively.

C. With nitric acid – ammonium nitrate.—A solution of 1 gm. (0.0038 mole) of acetoxymethyl dinitrotriazacycloheptane in a solution of 7.5 gm. (0.094 mole) of ammonium nitrate in 5.6 cc. (0.14 mole) of 99% nitric acid was let stand one day, then poured into ice and filtered to remove 0.12 gm. of impure trinitrotriazacycloheptane (m.p. 149° to 162° C.). This 13% crude yield was purified from acetone – petroleum ether (b.p. 60° to 70° C.) to melt at 166° C. A mixed melting point with authentic material was not lowered.

Liberation of Ethylenedinitramine by Alkaline Hydrolysis

A 1 gm. quantity of the nitramine to be analyzed was suspended in 12 cc. (0.015 mole) of 5% aqueous sodium hydroxide and boiled for 20 min., at which time decomposition was complete. The hydrolyzate was acidified to pH 1–2 with concentrated hydrochloric acid. After 12 hr. at 6° C., the precipitated ethylenedinitramine was filtered, water-washed, and dried at 110° C. The acid filtrate was evaporated to dryness under 12 mm. and a further yield was extracted from the residue with acetone and thus recovered upon evaporation. The total ethylenedinitramine was then weighed and its melting point found to be 175° to 177° C., in all cases.

Under these conditions ethylenedinitramine was itself recovered in 97% yield, while methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane, V, produced 98% of that amount expected on the basis of the structure. On the other hand 1,8-diacetoxy-2,5,7-trinitro-2,5,7-triazaoctane, VII, yielded only 82% of the expected ethylenedinitramine, while 1,3,6-trinitro-1,3,6-triazacycloheptane gave none at all.

Monomethylethylenedinitramine

A solution of one mole ethylenedinitramine in 2 moles of aqueous 40% formalin was treated with a drop of pyridine and 3.5 moles of acetic acid. After two hours at 25° C., a 67% yield of crude monomethylethylenedinitramine separated, m.p. 124° to 126° C.

When an excess of formaldehyde was used, the same product was obtained. Through a solution of 15 gm. (0.1 mole) of ethylenedinitramine in 40 cc. of

ethanol was bubbled 12 gm. (0.4 mole) of gaseous formaldehyde from paraform. When the temperature had subsided, the solution was cooled to yield 4.6 gm. of product, m.p. 126° C. Evaporation of the ethanol left 12.7 gm. more of product. The whole was crystallized from water at 80° C. to give 91% yield, m.p. 127° C. Calc. for $C_3H_8N_4O_5$: C, 20.0; 4.44; N, 31.1%. Found: C, 20.1; H, 4.43; N, 31.0%.

Prolonged heating in water caused evolution of formaldehyde. Attempted crystallization from hot acetone or methyl, ethyl, and butyl alcohols yielded only ethylenedinitramine. The compound is insoluble in ether, chloroform, methyl, or ethyl alcohol but is moderately soluble in acetone.

All variations of these two methods have failed to yield a compound identifiable as dimethylolethylenedinitramine, I.

1,5-Dinitro-3-oxa-1,5-diazacycloheptane, II

A solution of 0.15 gm. (0.001 mole) of ethylenedinitramine in 0.15 cc. (0.002 mole) of 40% formalin was treated at 20° C. with 0.015 mole (1.5 cc.) of acetic anhydride. The resulting solution warmed to 35° C. on standing at room temperature. It was then digested at 65° C. for 25 min., diluted with 8 cc. of water and the precipitate filtered, water-washed, and dried at 50° C. Weight of product was 45 mgm., m.p. 145° to 148° C. (shrinkage 72° C.). Yield calculated as crude 3,6-dinitro-1-oxa-3,5-diazacycloheptane was 23% of theory (ethylenedinitramine basis). Three crystallizations from warm acetone – petroleum ether solution raised the melting point to 154°–155° C. Calc. for $C_4H_8N_4O_5$: C, 25.0; H, 4.17; N, 29.2%. Found: C, 25.7; H, 4.46; N, 29.1%.

N,N'-Diacetoxymethylethylenedinitramine, III

A solution of 15 gm. (0.1 mole) of ethylenedinitramine in 16.25 cc. (0.2 mole) of 40% formalin was prepared by solution at 60° C. To this was added 9 gm. (0.11 mole) of sodium acetate and 60 cc. (0.57 mole) of acetic anhydride. The resulting slurry was digested at 65° C. for one hour. Dilution with 250 cc. of water precipitated 18.2 gm. overnight, m.p. 78° to 80° C. or 63% of theoretical. Crystallization from ethanol – petroleum ether raised this melting point to 83° C. Calc. for $C_8H_{14}N_4O_8$: C, 32.6; H, 4.77; N, 19.0%. Found: C, 33.0; H, 4.72; N, 18.9%.

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

V. 1,7-DINITROXY-2,4,6-TRINITRO-2,4,6-TRIAZAHEPTANE AND RELATED COMPOUNDS¹

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Abstract

When hexamethylenetetramine is nitrolyzed with nitric acid and an anhydride in absence of ammonium nitrate the synthesis of cyclic nitramines is decreased and the yields of esterified linear tetramethylenetrinitramines are increased. The two remaining carbon atoms and one nitrogen atom in hexamine can be accounted as esterified dimethylolnitramide. The isolation of a trace of linear pentamethylenetetranitramine from a normal nitrolysis of hexamethylenetetramine shows that in all of these reactions a common intermediate, dimethylolaminomethyldinitrotriazacyclohexane, must be present. This has never been isolated, but its reactions can be deduced from the behavior of methylene-bis-3,5-dinitro-1,3,5-triazacyclohexane.

The normal Hale nitrolysis of hexamine with 99.6% nitric acid (8) yields chiefly Cyclonite and dimethylolnitramine (6). It has been shown (9) that if the nitrolyzing agent, nitric acid, is supplemented by an acid anhydride, the course of nitrolysis can be changed in the case of 1,5-*endomethylene*-3,7-dinitro-1,3,5,7-tetrazacyclooctane (DPT), unless ammonium nitrate is present. We sought to test the theoretical consequences of this variation on hexamine itself.

Bachmann (3) has found that when hexamine is treated at room temperature with a mixture of nitric acid and acetic anhydride (1 : 1.2 moles) no Cyclonite is formed, but a fair yield of compound is produced for which the structure 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III, was proposed (11).

When the ratio of nitric acid to acetic anhydride is changed to 1 : 0.45 (nitric now being in excess) a low yield of Cyclonite is now formed, but it contains an impurity, not III, and too unstable for easy isolation. The impurity can, however, be converted to 1-acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V, by boiling in ethanol. The previous demonstration (9) that the nitroxymethylenenitramine linkage ($\text{NO}_2\text{CH}_2\text{—N—NO}_2$) is easily convertible to alkoxymethylenenitramine ($\text{RO—CH}_2\text{—N—NO}_2$) thus designates the impurity as 1-acetoxy-7-nitroxy-2,4,6-trinitro-2,4,6-triazaheptane (pro-V).

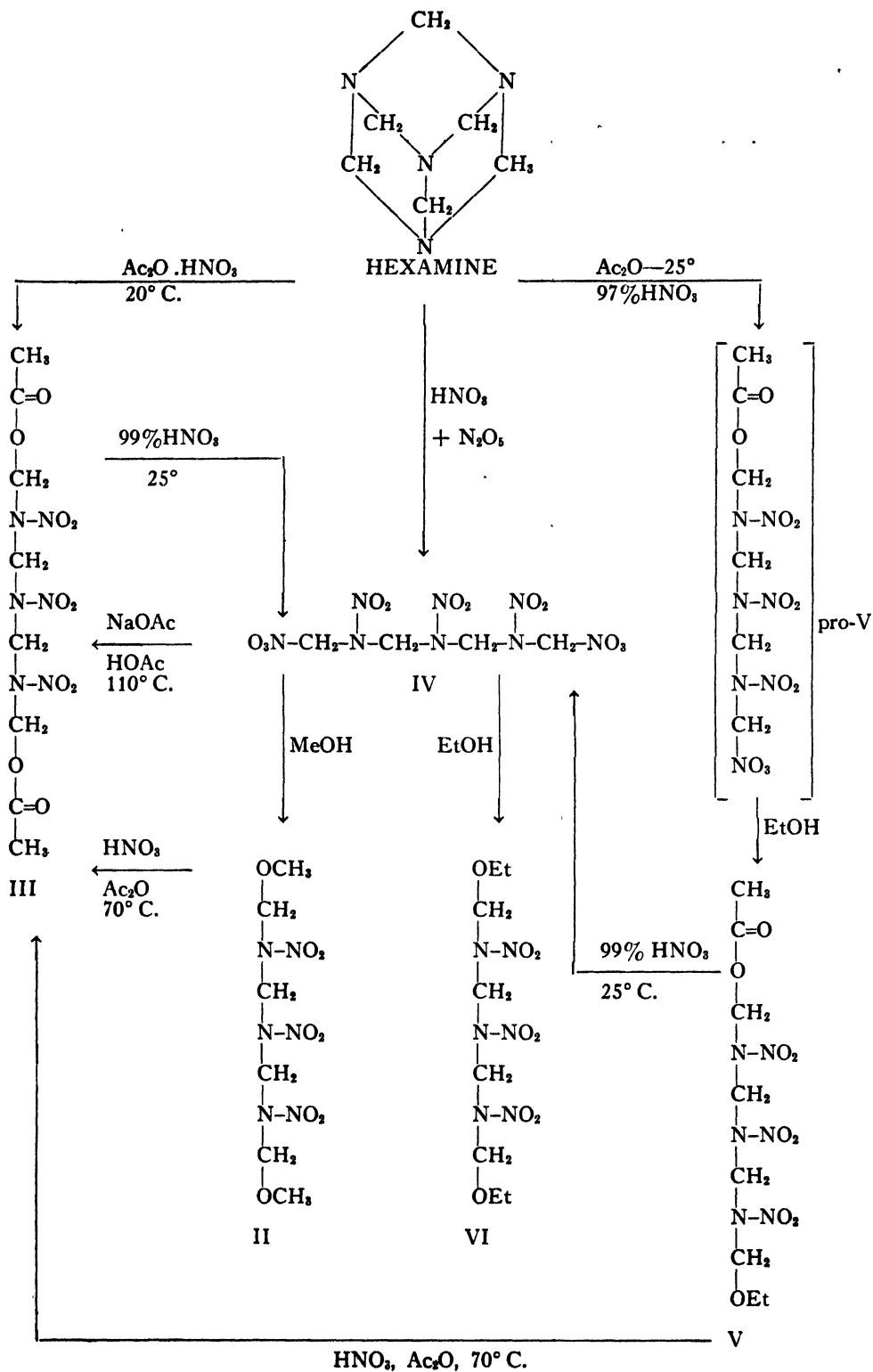
When either the 1,7-diacetoxy compound III or the 1-acetoxy-7-ethoxy compound V is treated with nitric acid, it is converted to 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV. The identity of this compound follows from its conversion to either 1,7-dimethoxy-(II) or 1,7-diethoxy-2,4,6-trinitro-2,4,6-triazaheptane (VI) by heating with the appropriate alcohol. The

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dinitroxy compound IV can also be converted to the diacetoxy compound VII by the sodium acetate-acetic acid treatment previously described (9). Finally, II and VI can be converted to the diacetoxy compound III by treatment with acetic anhydride containing enough nitric acid to oxidize the alkoxy radicals. Advantage has therefore been taken of the easy interconvertibility of nitraminomethylene ethers and esters to establish an interrelated series of compounds of identical skeletal type.

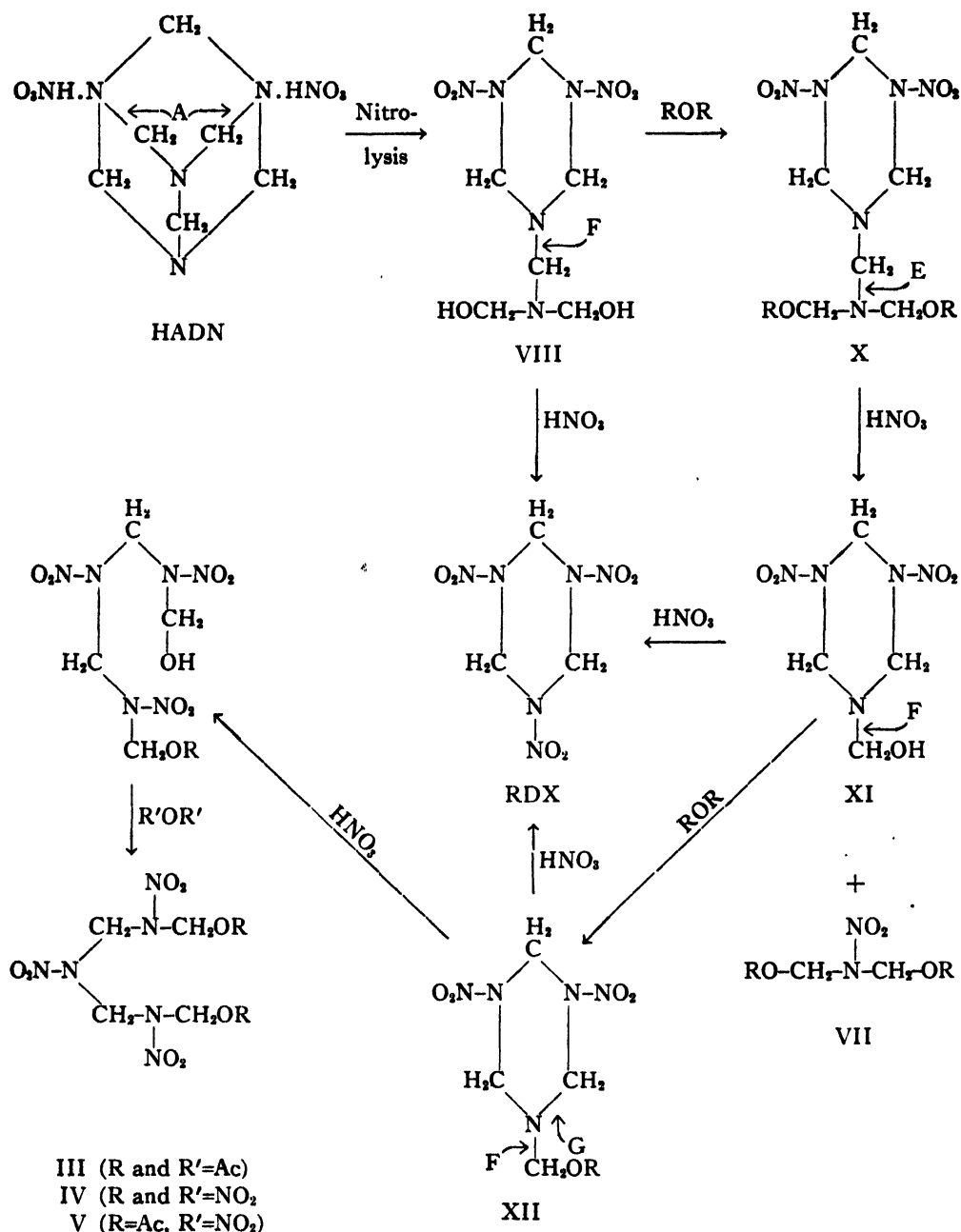
When hexamine is treated with the nitric acid-nitrogen pentoxide mixture equivalent to nitric acid with apparent strength of 106%, the yield of Cyclonite is lowered appreciably. This is not owing to a destructive action of the pentoxide, because a normal nitrolysis, to which nitrogen pentoxide is subsequently added, gives a normal yield of Cyclonite (and DPT, on neutralization) with little other by-product formation.

The Cyclonite produced from the 106% nitric acid contains an unstable impurity, which must be 1,7-dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane IV, because cooking with methanol produces a 22% yield of 1,7-dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane, II.

Three nitrolyses of hexamine have thus been outlined which yield esters when anhydrides are present. In two of these no other compound indicative of reaction mechanism could be isolated, probably because of difficulty in manipulation of the unstable and dangerous complex reaction product. The third, however, which converted hexamine to 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III, in 51% yield, also produced a 39% yield (1:1 basis) of diacetoxydimethylnitramide VII in spite of some decomposition during distillation. We assume that III and VII were present approximately in equimolar amounts.

It is evident that the tetramethylenetriamine skeleton is formed in all three reaction mixtures containing anhydride. The following scheme suggests how this tetramethylenetriamine structure is formed.

The first nitrolyses at A would yield the intermediate VIII, which in absence of anhydride would undergo demethylation and, finally, nitrolysis at F to give Cyclonite (RDX). In presence of anhydrides, however, the free hydroxyl groups in VIII would tend to be esterified to form X. This esterification would hinder demethylation. The isolation of VII in the preparation of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III ($R, R' = \text{Ac}$), indicates that the next nitrolysis occurs at E in X to leave the compound XI. The latter has been reported as its ethyl ether (evidently via the nitrate ester) in low temperature nitrolysis of hexamine (5), but its survival in the anhydrous reaction mixture would not be expected; it would either nitrolyze at F to give Cyclonite (RDX) with demethylation, or else it would esterify in presence of anhydride to give XII. This esterification would hinder demethylation and permit the final attack by nitrolysis at G to open the ring. Subsequent esterification would yield one of the three compounds III, IV, and pro-V which are produced by reaction mixtures rich in anhydride.



Compounds VIII, X, and XI have never been isolated. Some evidence (5) indicates more than a transient existence of XII in hexamine nitrolyses. The behavior of a compound first suspected to be XI but which actually is methylene-*bis*-1-[3,5-dinitro-1,3,5-triazacyclohexane], XVII, may, however, contribute some understanding to the chemistry of these hypothetical transients. Compound XVII was first prepared by Vroom and Winkler (13) and later by Bevan, Carruthers, Dunning, Foss, Jones, and Sullivan (5) by decomposition of the free base of 3,5-dinitro-3,5-diazapiperidinium nitrate (PCX) (13). This

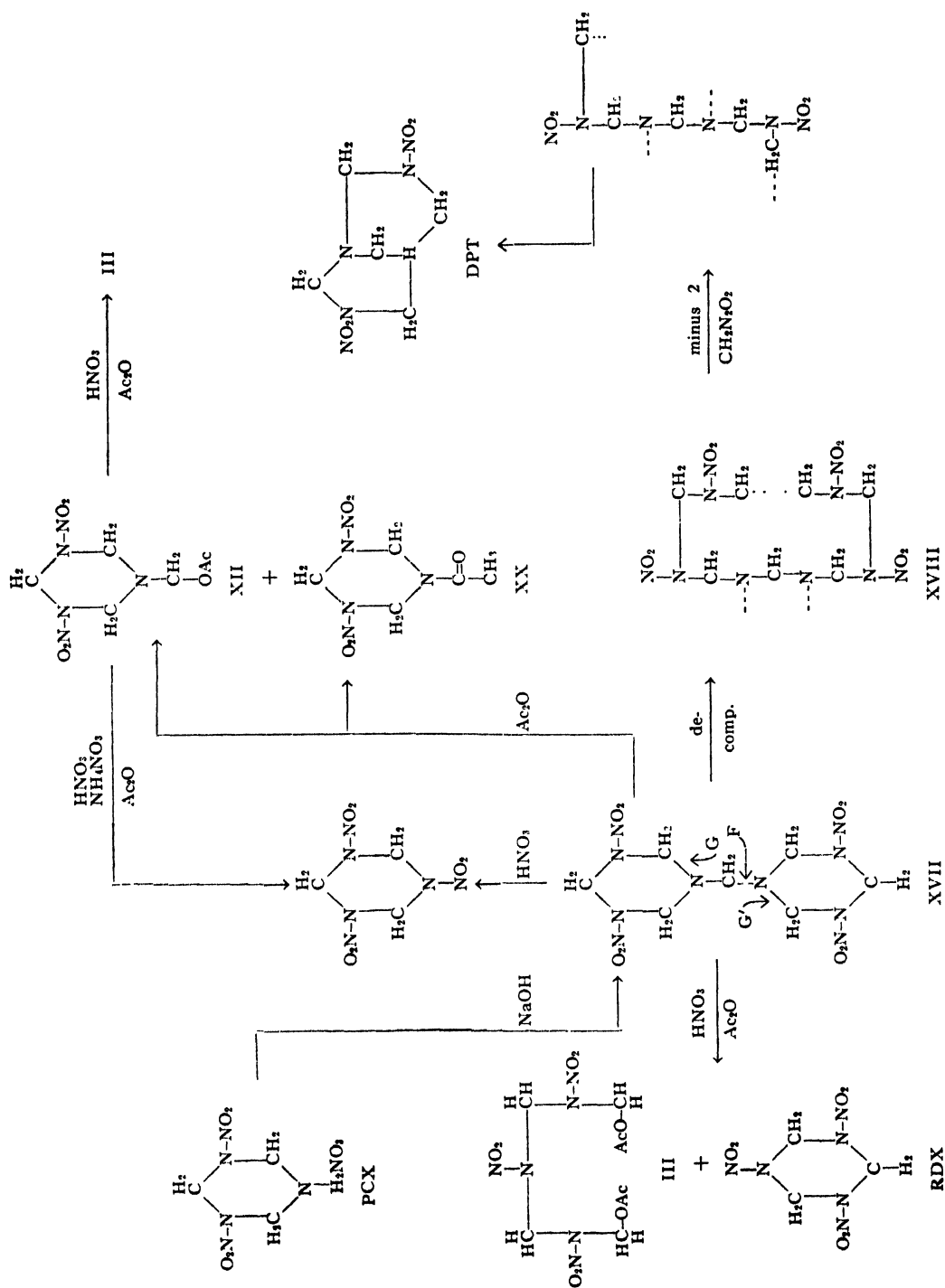
decomposition evidently involves decomposition of part of the PCX base to formaldehyde at such a rate that it can condense with more amine to give XVII. The constitution of the product was first recognized in the present work by its elemental analysis for nitrogen and by a molecular weight determination of a value, 320, which was closer to 360 (calculated for XVII) than was 207 (calculated for XI). The earlier workers (5) had ascertained the existence of the cyclotrimethylenetriamine cycles by conversion to 1-aceto (1), XX, and 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (4) but these methods did not produce 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII (R=Ac), which ought to result by acetolysis of XVII. It has now been found that XII (R=Ac) cannot be isolated by a slow acetolysis at 25° C., but a rapid reaction (five minutes) at 85° C. yields 47% of the expected yield of this compound from XVII in addition to a 28% yield of XX. This behavior is analogous with the acetolysis of methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane (10) to 1-aceto-3,6-dinitro-1,3,6-triazacycloheptane and 1-acetoxymethyl-3,6-dinitro-1,3,6-triazacycloheptane.

Confirmation for the structure of XII (R=Ac) was afforded by its conversion to the known 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (5) by boiling in ethanol and by its nitrolysis either to 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazahexane with acetic anhydride and nitric acid or to RDX with nitric acid, acetic anhydride, and ammonium nitrate. These results are comparable with those obtained by the nitrolytic scission of XVII (at F and G) which yielded RDX and 1,7-diacetoxy-2,4,6-triazahexane with acetic anhydride and nitric acid, but only RDX when ammonium nitrate was included in the nitrolysis reagent.

The weakness of the bonds at G relative to those at F is indicated by the thermal decomposition of XVII to 1,5-dinitro-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane (DPT). This can be illustrated as passing through the intermediate XVIII formed by initial scission at G,G'. Subsequent loss of the elements of methylenenitrimine,* followed by recombination, would produce DPT.

The behavior of compounds XII and XVII indicates that the bond strengths at F and G must both have low values relative to the other linkages in this type of compound. Under these circumstances it might be expected that compounds such as VIII, X, XI, and XII would not be isolable from the nitrolysis of hexamine. The chemical reactions of XII and XVII show analogously that the type of product which terminates the reaction sequence VIII → XII inclusive will depend on the decrease in stability of linkage F relative to that of the normally weaker bond at G. This decrease in stability will

* No evidence has ever been forthcoming to indicate that methylenenitrimine can cyclize to form Cyclonite. In the present instance no Cyclonite could be detected after the crude DPT was destroyed with hot 70% nitric acid.



produce Cyclonite rather than any one of the linear products and seems to be brought about by ammonium nitrate, which acts to prevent esterification during the reaction sequence VIII \longrightarrow XII.

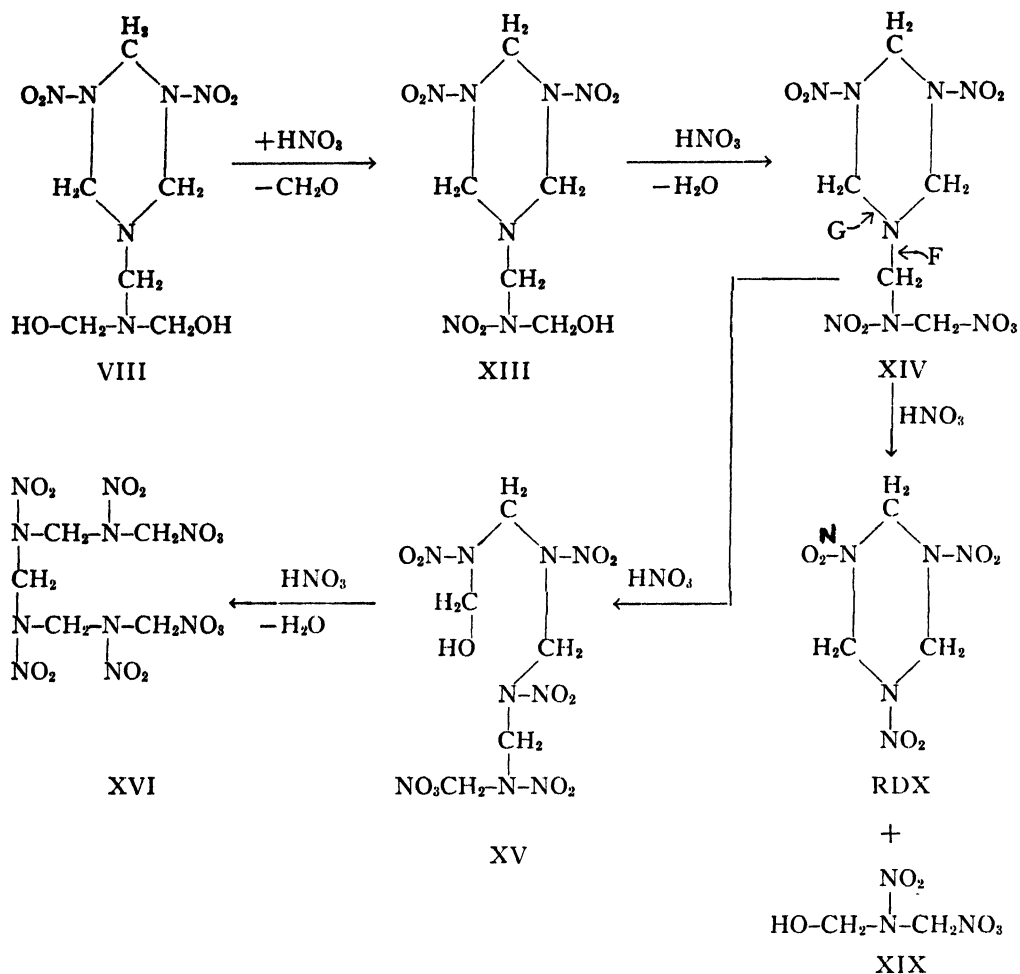
It is not to be expected that the reaction follows rigorously the indicated courses. Firstly esterification is known to occur in presence of anhydrous acids as an equilibrium reaction. Secondly esterification can be a slow process, and a competing reaction such as nitrolysis can overtake it. Indeed the yields which are obtained do not justify this mechanism as absolute, but only as preponderant.

Evidence for the simultaneous occurrence of pure nitrolysis and nitrolysis-esterification has been found in connection with the so-called anhydride processes for preparation of Cyclonite (2, 12). The course of both these methods can be considered, in the principal stage, as the reaction path HADN \longrightarrow VIII \longrightarrow RDX just outlined. Although an esterifying medium (acetic anhydride) is used, it is best maintained in proportionate minimal amount and the presence of ammonium nitrate undoubtedly promotes the demethylolation-nitrolysis phases. The main product is certainly Cyclonite. Nevertheless we have been able to isolate from the Bachmann reaction mixture (89% RDX + HMX yield) a 3% yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane III and a 1% yield of diacetoxydimethylnitramide VII (6). From the Schiessler-Ross reaction mixture, these yields were 3% of III and 4.5% of VII.

One is tempted to draw a similar conclusion from an observation connected with the Hale hexamine nitrolysis where anhydride is, ostensibly, not involved. If the crude Cyclonite from such a nitrolysis is boiled in ethanol and the resulting solid is fractionally crystallized, a small amount of 1,9-diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane can be isolated. This is indicative of a slight esterification reaction to produce the 1,9-dinitroxy analogue, XVI. Its formation may be outlined as shown on p. 510.

According to this scheme, VIII first undergoes nitrolysis-demethylolation, but esterification of the product XIII occurs before a second demethylolation can occur. The resulting XIV can either nitrolyze at F to give Cyclonite (RDX) and hydroxy-nitroxydimethylnitramide, XIX, or it may nitrolyze at G to give XV which is then esterified to give XVI.

This latter mechanism is offered chiefly as an illustration of the complexity of the nitrolysis of hexamine rather than definitely to specify the mode by which XVI is formed. It must be recalled that compound XVI is produced in good yield by nitrolysis of DPT (9). The demonstrated presence of tetra-nitrotetrazacyclooctane, HMX, (4) in Hale Cyclonite indicates ephemeral presence of DPT. The trace of XVI which evidently is present in Hale Cyclonite could therefore have been formed by several alternative routes.



Experimental*

1,7-Dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane, II

A. From Hexamine

To a stirred solution maintained at 15°C . of 60 gm. (0.556 mole) of nitrogen pentoxide in 107 gm. (1.68 moles) of 99.8% nitric acid (titrated, 106% HNO_3) was added 20 gm. of hexamine (0.143 mole) over a 35 min. period. After 30 min. longer at 28°C . the mixture was poured into ice to precipitate a plastic mass. The aqueous diluate was neutralized with ammonia to yield 0.5 gm. of DPT, m.p. 187° to 200°C .

The plastic mass was unstable, so was immediately triturated with 300 cc. methanol in four portions. The Cyclonite was filtered off and the filtrate boiled down to one-quarter volume to yield, on filtration, a second crop of this substance, total weight 14.1 gm. or 44.5% of theoretical. The remaining methanol filtrate was poured into water to yield a semisolid oil which was extracted with 15 cc. carbon tetrachloride. The carbon tetrachloride slurry after one day was filtered. The solid was re-eluted with carbon tetrachloride.

* All melting points have been corrected against reliable standards.

finally to leave 13.2 gm. of product, m.p. 70° to 103° C. This material was separated by water-ethanol crystallization into 9.3 gm., m.p. 100° to 104° C. and a remainder m.p. 60° to 70° C. The latter was not further investigated. It ought to contain dimethoxydimethylnitramide.

The less water-ethanol soluble 9.3 portion (22% yield, 1 : 1 basis) contained some residual Cyclonite from which it was freed by repeated crystallization from water-ethanol, then benzene-petroleum ether (b.p. 60° to 70° C.) and finally from carbon tetrachloride. It then melted at 104° to 105° C. Calc. for $C_6H_{14}N_8O_8$: C, 24.2; H, 4.62; N, 28.3%. Found: C, 24.3; H, 4.63; N, 28.5%.

The molecular weight (Rast) was 276 to 291 (calc. 298) in camphor. The compound is soluble in acetone and benzene, moderately soluble in dioxane, methanol, and ethanol. It is difficultly soluble in petroleum ether (60° to 70° C.), ethyl ether, carbon tetrachloride, and water, and is best crystallized from the latter two solvents. It is slowly decomposed by hot ammonia and hot alkali. Its nitramine linkages are attested by decomposition in concentrated sulphuric acid and by a positive Franchimont test. Decomposition by the Kjeldahl method gives 13.1 to 13.3% nitrogen (Cyclonite gives 9.4 to 9.8%) while distillation from 30% alkali gives 5.3 to 5.4% basic nitrogen in the distillate.

When the nitrolysis procedure was altered by addition of the nitrogen pentoxide *after* the addition of hexamine, the results were radically different. A normal 82% yield (26.4 gm.) of Cyclonite was obtained and only 0.85 gm. of the 1,7-dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane. Furthermore the yield of DPT obtained on neutralization of the aqueous filtrate was normal (3.13 gm.) at 10% of theoretical (1 : 1 basis).

B. From 1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV

A suspension of 0.1 gm. (2.8×10^{-4} mole) of IV in 3 cc. of absolute methanol dissolved during five minutes' boiling. The solvent was evaporated to a small volume and the remainder was crystallized from aqueous ethanol (1 : 2.3) to melt at 103° to 104° C. with 60% recovery. Its mixed melting point with the material from hexamine was not lowered.

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III

A. From 1,7-Dimethoxy-2,4,6-trinitro-2,4,6-triazaheptane

A solution of 0.03 gm. (1×10^{-4} mole) of II in 0.33 cc. (8×10^{-3} mole) of 99% nitric acid and 0.5 cc. (5×10^{-3} mole) of acetic anhydride was heated 30 min. at 70° C. with some evolution of brown fume. After precipitation with ice and water, the crude III was filtered by suction (wt. 30 mgm., 84% of theory) and its melting point 148° to 149.5° C. was raised to 155° to 156° C. by crystallization from ethanol-water and then from carbon tetrachloride with 70% loss. A mixed melting point with material prepared according to Bachmann (3) was not lowered. Calc. for $C_8H_{14}N_6O_{10}$: C, 27.2; H, 3.96; N, 23.8%. Found: C, 27.3; H, 3.74; N, 23.8%.

B. From 1,7-Nitroso-2,4,6-trinitro-2,4,6-triazaheptane, IV

A solution of 0.06 gm. (1.66×10^{-4} mole) of IV and 0.05 gm. (7×10^{-4} mole) of sodium acetate in 1 cc. of acetic acid was boiled for three minutes. Crystallization was effected after cooling by addition of 10 volumes of water. The precipitate (0.045 gm., 76% yield) melted at 154° to 155° C.; mixed melting point with material from the previous preparation was not lowered.

C. From 1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

After a solution of 0.66 cc. (0.016 mole) of 99% nitric acid and 1.02 cc. (0.01 mole) of acetic anhydride had been heated to 70° C., 60 mgm. (0.17×10^{-3} mole) of V was mixed in. After 30 min. at this temperature (nitrogen oxide evolution) the whole was poured into ice and water. The impure solid (m.p. 134° to 137° C., 88% if it had been pure) was repeatedly crystallized from acetone to melt at 154° to 155° C. A mixed melting point with material by methods A and B was not lowered.

D. From Hexamine

Acetic anhydride, 120 cc. (1.22 mole), was placed in a flask and maintained at 20° C. with an ice bath while 44 cc. (1 mole) of 99% nitric acid was added to it with stirring. To this solution was added a solution of 33.6 gm. (0.24 mole) of hexamine in 55 cc. (0.97 mole) of acetic acid over a period of 30 min. at 15° to 20° C. The suspension was then warmed to 75° C. and cooled to 15° C. while 40 gm. (0.5 mole) of 50% aqueous sodium hydroxide was added dropwise with cooling. The reaction mixture was then cooled to 5° C. and the precipitate filtered off and washed with 100 cc. of acetic acid. Weight of crude III was 50.8 gm., m.p. 133° to 135° C. Yield calculated as crude is 60% of theory (1 : 1 mole basis). This can be purified further by crystallizing from acetic acid whereby the yield of almost pure diacetoxytrinitrotriazaheptane is 51% of theory, m.p. 153.5° to 154° C.

The reaction filtrate and the acetic acid washings, to which 100 cc. of acetic anhydride was added to keep the solution anhydrous, were concentrated by distilling off the acetic acid under reduced pressure. The residue obtained in this way was extracted with ether and found to contain 19.1 gm. of almost pure diacetoxydimethylnitramide (VII), b.p. 151° to 160° C. at 12 to 13 mm. pressure. The refractive index of this liquid was 1.4527 at 25° C. (6). Yield calculated on the basis of 1 mole of hexamine giving 1 mole of VII was 39% of theory.

There seemed to be some loss of VII owing to decomposition during the distillation, and the final yield obtained did not therefore represent the total amount of VII formed in the reaction.

E. From 1-Acetoxyethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII

A solution of 1.05 ml. (0.025 mole) of 99% nitric acid in 5 ml. (0.05 mole) of acetic anhydride was treated at 25° C. with 1.25 gm. (0.005 mole) of XII. The warm solution was further heated to 50° C. for one-half hour, then cooled, diluted, and filtered to yield 1.65 gm., m.p. 144° to 148° C. Crystallization

from hot acetic acid yielded 1.43 gm., m.p. 152.5° to 154° C. Since a mixed melting point with III prepared otherwise was not lower, the yield is 81% of theoretical. No RDX was detectable after destruction of the product with hot 70% nitric acid.

1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

As an alternative variation of the RDX preparations, hexamine was treated with nitric acid and acetic anhydride at -25° C. A solution was prepared at -25° C. by slow addition of 306 gm. (4.86 moles) of 99 to 100% nitric acid to 222 gm. (2.15 moles) of acetic anhydride. To this stirred solution at -25° C. was added 20 gm. (0.143 mole) of hexamine over a 90 min. period. The reaction mixture contained white solid. After an additional 30 min. the mixture was poured into 1600 gm. of ice and water. The precipitate was filtered and washed neutral to bromocresol green paper. The vacuum dried weight was 30.5 gm., m.p. 135° to 138° C.

Oxidation of this crude product with hot 70% nitric acid showed that it contained 24% of RDX, m.p. 203° to 204° C., a yield of 7.3 gm. or 23% of theoretical. Twenty grams of the crude product was extracted thrice with 60 cc. portions of boiling 95% ethanol to give 8.6 gm. of material, m.p. 95° to 110° C., but not clear until 130° C. The estimated yield at this point was 15%. This material was crystallized eight times from either ethanol-water, benzene-petroleum ether (60° to 70° C.) or carbon tetrachloride until a constant melting point of 106° to 107° C. was obtained. Complete destruction of this material with hot 70% nitric acid showed that no RDX was present. After hydrolysis with alkali it gave a positive acetate test with lanthanum nitrate. The compound gave a positive Franchimont nitramine test. Calc. for $C_8H_{16}N_6O_9$: C, 28.5; H, 4.71; N, 24.7; CH_3CO , 12.7%. Found: C, 28.3; H, 4.76; N, 24.9; CH_3CO , 13.4%.

The compound gave a positive nitramine test and reduction with sodium amalgam gave a salicylaldehyde spot test for hydrazine (Feigl). Hydrolysis with dilute sulphuric acid gave no hydroxylamine. The compound decomposed in boiling 6% hydrochloric acid after 30 min. to give no water insoluble residue. The solution thus obtained from 0.3435 gm. in 8.5 cc. of 6% hydrochloric acid gave duplicate yields of formaldehyde-dimedone derivative (7) which checked within 0.5% and corresponded to 0.1144 gm. formaldehyde. This represents 13%, or half, of the carbon in the original sample.

1,7-Dinitroxy-2,4,6-trinitro-2,4,6-triazaheptane, IV

A. From 1-Acetoxy-7-ethoxy-2,4,6-trinitro-2,4,6-triazaheptane, V

To 0.6 cc. of 99% nitric acid at 0° C. was added 80 mgm. (2.4×10^{-4} mole) of V. After warming to 20° C. over 20 min. and then drowning in water a 65 mgm. yield was obtained of material, m.p. 145° to 146° C., (crude yield 77%). This was crystallized from 1:1 dioxane-carbon tetrachloride to melt at 153° to 154° C. (35% pure yield).

B. From 1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III

After 1.00 gm. (2.8×10^{-3} mole) of III was added to 8 cc. (0.19 mole) of 99% nitric acid at 0° C., the clear solution after one hour at 20° C., was drowned in 12 volumes of ice and water. The crude precipitate (91% of theoretical) was dissolved in 8 cc. dioxane at 20° C. and 8 cc. of carbon tetrachloride was added at once. The crystals melted at 151.5° to 152° C. (0.55 gm. or 54% of theoretical). Two subsequent crystallizations raised the melting point to 154° C. (decomp.) when inserted into the rising bath at 148° C. Mixed melting point with product from preparation A was not lowered but with III it was lowered to 147° C. (insertion at 146° C.). The material is a powerful explosive very sensitive to impact when pure. Calc. for $C_4H_8N_8O_{12}$: C, 13.3; H, 2.24; N, 31.2%. Found: C, 13.7; H, 2.33; N, 31.6%.

The compound is destroyed by prolonged contact with water.

1,7-Diethoxy-2,4,6-trinitro-2,4,6-triazaheptane, VI

A suspension of 0.17 gm. (4.7×10^{-4} mole) of IV in 4 cc. of 99% ethanol was refluxed for 25 min. Dilution with 10 cc. water precipitated 80 mgm. 52.2% of theoretical of product, m.p. 79° to 80.5° C. Two crystallizations from aqueous ethanol (1 : 2.3) did not raise the melting point. Calc. for $C_8H_{18}N_6O_8$: C, 29.4; H, 5.58; N, 25.8%. Found: C, 29.6; H, 5.60; N, 26.1%.

*1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane, III**A. From Schiessler-Ross Synthesis of Cyclonite*

To a solution of 57 cc. (1.0 mole) of acetic acid in 246 cc. (2.6 moles) of acetic anhydride at 70° C. was added with stirring, simultaneously and equivalently, a mixture of 80 gm. (1 mole) of ammonium nitrate and 30 gm. (1 mole) of Roessler and Hasslacher paraform over a period of 25 min. The temperature during the addition was maintained at $70^\circ \pm 2^\circ$ with slight cooling required. The reaction mixture was stirred 20 min. longer at 65° to 70° C., cooled to 35° C., diluted with 300 cc. water, cooled to 10° C., and filtered. Weight of product was 38.6 gm., m.p. 196° to 198° C. (shrinkage 195° C.). Yield calculated as crude Cyclonite was 52.3% of theory (formaldehyde basis). This was found to contain 89% of pure RDX-HMX on "fume off" with 70% nitric acid.

Although the crude Cyclonite contained some III, only the products in the acid filtrate were examined. The acetic acid filtrate was neutralized to pH 6 with 28% aqueous ammonia and the water distilled off under reduced pressure. The residue from the distillation was allowed to cool until it had completely solidified. The water insoluble products were removed by swirling the solid cake in water and filtering off the undissolved material. This gummy solid was dissolved in 25 cc. of acetone and the solvent then evaporated almost to dryness under a stream of air. The solid product obtained in this manner was not sticky; weight was 5.07 gm. It was separated by crystallization from acetone, ethanol, ethyl acetate, acetic acid, and water into the

following product; quantities are based on per cent of theoretical on the formaldehyde basis:

1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	2.1%
1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane	1.1%
1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	2.8%
Cyclonite and HMX	traces

B. From Bachmann Synthesis of Cyclonite

The synthesis of Cyclonite by this method is described below. Essentially the same separation as that outlined above gave a 3% yield of III and only traces of the other compounds.

Diacetoxymethylhydrazine, VII, from Anhydride Processes

A. From Schiessler-Ross Synthesis of Cyclonite

To a solution of 228 cc. (4 moles) of acetic acid in 984 cc. (10.4 moles) of acetic anhydride were added at 70° C. with stirring, a finely ground mixture of 120 gm. (4 moles) of Roessler and Hasslacher paraform and 320 gm. (4 moles) of ammonium nitrate over a period of 27 min. The reaction mixture was stirred 20 min. longer at 70° C., cooled to 15° C., and 240 gm. (3 moles) of 50% aqueous sodium hydroxide was added dropwise while the temperature was held below 20° C. The heavy sludge thus formed was cooled to 0° C. and filtered. The filter cake was washed with 200 cc. of acetic acid which was added to the acid filtrate. The weight of this precipitate was 146 gm., m.p. 184° to 188° C.; yield calculated as crude RDX-HMX is 50% of theory (formaldehyde basis).

The acid filtrate was concentrated by distilling off the acetic acid at 11 mm. pressure. The sludge which remained was extracted with three 400 cc. portions of ether. The ether extracts were concentrated under a pressure of 12 mm. to an oily residue which was suspended in 250 cc. water and the resulting sticky emulsion was neutralized to pH 8 with sodium carbonate and then extracted again with five 150 cc. portions of ether. The ether extracts were dried over sodium sulphate. The ether was removed by distillation under reduced pressure. A yellow oil remained which was distilled by flash distillation at a pressure of 12 mm. This method was used since the oil was contaminated with other products which decomposed violently when all the material was distilled at one time. In distilling, the oil was added dropwise from a separatory funnel to a 25 cc. Claisen flask which was immersed in an oil bath at 200° to 215° C. A pressure of 12 mm. was maintained in the system by regulating the addition of the oil. Each drop was allowed to distill over before the next drop was added in order to avoid an explosion. The distillate collected in this way smelled strongly of formaldehyde owing to decomposition during the distillation, so it was suspended in 60 cc. of water and neutralized to pH 7.5 to 8 with sodium carbonate and again extracted from the water with three 40 cc. portions of ether. The ether extracts were dried over sodium sulphate, then the solvent was removed and the oily residue

distilled at 12 mm. The fraction boiling at 153° to 156° C. at 12 mm. (weight 6.0 gm.) was almost pure diacetoxymethylhydrazine (VII). It was identified as such by analysis (elemental), refractive index, and by nitration with 99% nitric acid whereupon it gave a 38% yield of dinitroxymethylhydrazine, identified by mixed melting point with an authentic sample. The crude yield of VII was 2.4% of theory (formaldehyde basis) while the yield of pure material, b.p. 153° to 156° C. at 12 mm. was 1.5%.

B. From Bachmann Synthesis of Cyclonite

A Bachmann Cyclonite reaction, rich in acetic anhydride, was carried out by adding a solution of 33.6 gm. (0.24 mole) of hexamine in 160 cc. (2.8 moles) of acetic acid and a solution of 38.4 gm. (0.48 mole) of ammonium nitrate in 41 cc. (0.96 mole) of 99% nitric acid, simultaneously to 226 cc. (2.4 moles) of acetic anhydride at 69° ± 1° over a period of 22 min. Throughout the addition a 90 sec. lead of nitric acid : ammonium nitrate was maintained. The suspension was stirred 15 min. longer after the addition at 70° C., then cooled to 20° C. and 30 gm. (0.37 mole) of a 50% aqueous sodium hydroxide solution was added, keeping the temperature below 20° C. The resulting slurry was cooled to 5° C. and the precipitate filtered, washed with 150 cc. of acetic acid, and dried at 50° C. Weight of Cyclonite was 66.5 gm., m.p. 187° to 192° C. The acid filtrate, together with the acetic acid washings, was concentrated under reduced pressure and the diacetoxymethylhydrazine was isolated as in the Ross reaction (described above). A further 7.6 gm. of crude Cyclonite was obtained during the working up of the filtrate. The total crude yield of Cyclonite was then 74% of theory (2 : 1 mole basis). The yield of relatively pure VII obtained was 0.5 gm., b.p. 150° to 155° C. at 11 mm. The refractive index at 25° C. was 1.4526. Yield is 1.0% on basis of 1 mole of hexamine giving 1 mole of VII.

When the usual Bachmann reaction was carried out where the hexamine : nitric acid : ammonium nitrate : acetic acid : acetic anhydride molar ratio was 1 : 4.18 : 2.54 : 11.6 : 7.1, a 0.9% yield of crude VII was obtained, b.p. 147° to 160° C. at 12 mm.

Methylene-bis-1-[3,5-dinitro-1,3,5-triazacyclohexane]

A ground suspension of 24 gm. (0.1 mole) of 3,5-dinitro-3,5-diazapiperidinium nitrate (13) in 60 cc. acetone was maintained at 5° to 7° C. and stirred while 0.1 mole (60 cc.) of 6.6% aqueous sodium hydroxide was added over 25 min. The pH did not exceed 5.6. The mixture was then filtered to yield a precipitate which weighed 9.3 gm. after fivefold washing with cold water, twofold washing with ethanol, and finally with ether. This crude yield, melting at 130.5° to 131° C. was, then, 50.7% of theoretical. Any contaminating RDX could be removed by centrifugation of this crude material, finely ground, in an ethylene dibromide - petroleum ether (b.p. 90° to 100° C.) mixture of density 1.71 to 1.72. The portion less dense than this medium was dissolved in 70 cc. nitromethane, filtered, and the filtrate treated with 140 cc. of dry ether. This yielded 7.1 gm., m.p. 132.6° to 132.8° C. of

pure material, or 39% of theoretical. The product yielded no Cyclonite after digesting with hot 70% nitric acid. An alternative purification involved solution in 200 cc. acetone with subsequent crystallization after dilution with 100 cc. of petroleum ether (b.p. 40° to 60° C.). Calc. for $C_7H_{14}N_{10}O_8$: C, 22.95; H, 3.83; N, 38.3%. Found: C, 23.18; H, 4.25; N, 38.5%. The 10% discrepancy in the hydrogen value is typical of all results from the analysts (Arlington Laboratories) on all compounds containing the methylenenitramine linkage. The error may be minimized by slow burning of the sample and by admixture with potassium dichromate.

This compound was converted to 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane (4) in 49% yield (1 : 1 basis) when 0.105 gm. (2.9×10^{-4} mole) was dissolved in 1 cc. of acetic anhydride over 15 min. shaking. After 10 hours the solution was diluted with water, filtered after long hydrolysis, and neutralized to pH 6.5 with aqueous alkali. The precipitate weighed 30 mgm. and melted at 145° to 148° C. Crystallization from ethanol raised this melting point to 153° to 155° C., and a mixed melting point with an authentic sample was not lowered. Omission of the long period of hydrolysis lowered the yield markedly because of unworkable impurities.

1-Acetoxyethyl-3,5-dinitro-1,3,5-triazacyclohexane, XII

Acetolysis of XVII at room temperature over a long period of time caused by-product formation which obscured the principal reaction products. This by-product formation was minimized by addition at once of 25 gm. (0.0683 mole) of methylene-bis-dinitrotriazacyclohexane to 65 cc. (0.69 mole) of acetic anhydride and 80 cc. of acetic acid at 65° to 75° C. Solution was complete after two minutes. The temperature was maintained at 85° C. for four to six minutes and then lowered to -40° C. and allowed to warm slowly to 5° C. The crystalline precipitate was filtered and washed with petroleum ether (b.p. 60° to 80° C.). The product, m.p. 101° to 137° C., weighed 10.2 gm. or 60% of the expected yield of acetoxymethyldinitrotriazacyclohexane, XII. It was purified by solution in 70 cc. dry acetone from which it was precipitated by 80 cc. dry petroleum ether (b.p. 60° to 80° C.). Filtration at 0° C. yielded 8.0 gm. (47% of theory), m.p. 141° to 143° C. Repeated crystallization

XII. INTERPLANAR SPACING, Cu-K α RADIATION

<i>d</i> , <i>kX</i>	Relative intensity 1-10	<i>d</i> , <i>kX</i>	Relative intensity 1-10	<i>d</i> , <i>kX</i>	Relative intensity 1-10
9.05	9	3.30	6	2.43	3
6.64	8	3.15	9	2.37	3
6.05	8	3.04	7	2.32	4
5.63	10	2.92	4	2.25	1
5.06	8	2.83	2	2.17	1
4.54	7	2.77	4	2.06	1
4.20	7	2.67	1	1.99	1
3.91	7	2.59	8	1.95	1
3.57	9	2.53	2		

raised this melting point to 143.7° to 144.7° C. Calc. for $C_6H_{11}N_5O_8$: C, 28.9; H, 4.45; N, 28.1; CH_3CO , 17.3%. Found: C, 29.1; H, 4.39; N, 28.5; CH_3CO , 17.6%.

The filtrate from which XII was isolated was vacuum evaporated to dryness and the residue extracted with acetone at 25° C. to leave 6.8 gm. of an intractable, white material, m.p. 144° C. Evaporation of the acetone left a syrup from which 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, XX, m.p. 156° to 157° C., was obtained by five minutes boiling with water. Yield was 4.2 gm. or 28% of theoretical.

When 0.5 gm. (0.002 mole) of 1-acetoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane was dissolved in 4 cc. absolute ethanol over five minutes, the cooled solution yielded 0.17 gm. (36% of theory) of 1-ethoxymethyl-3,5-dinitro-1,3,5-triazacyclohexane (m.p. 110° to 111° C.). Purification from boiling ethyl ether raised the melting point to 114° to 117° C., dependent on rate of heating.

Conversion of acetoxymethyldinitrotriazacyclohexane, XII, to Cyclonite in 73% yield was effected by proportionate addition of 1.25 gm. (0.005 mole) of this compound and a solution of 0.26 gm. (0.0032 mole) of ammonium nitrate in 0.27 ml. (0.0065 mole) of nitric acid over 35 min. to 2.7 ml. (0.027 mole) of acetic anhydride and 1 ml. of acetic acid at 67° to 71° C. Initial addition of the solid was retarded 5% behind that of the nitric acid solution. Subsequent dilution by 75 ml. of cold water precipitated 1.08 gm., m.p. 139° to 196° C. When this crude product was boiled with 70% nitric acid, recovery of Cyclonite, m.p. 200° to 203° C. (softening at 197° C.) was 0.81 gm. Identity was authenticated by mixed melting point.

Nitrolysis of Methylene-bis-dinitrotriazacyclohexane

If 0.105 gm. (2.9×10^{-4} mole) of methylene-bis-dinitrotriazacyclohexane was suspended in 0.2 ml. (2×10^{-3} mole) of acetic anhydride plus 0.04 ml. (10^{-3} mole) of 98% nitric acid and warmed to 35° to 40° C., then chilled and maintained at 28° C. for one hour, a 35% yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane was obtained and identified by mixed melting point. Isolation involved drowning of the mixture in water. The precipitate was filtered off (m.p. 130° to 135° C., weight 0.13 gm.) and dissolved in hot acetic acid. The crystal crop of 0.05 gm. (78% of theoretical 1:1 basis) of Cyclonite, m.p. 200° to 202° C., was filtered off and identified by mixed melting point. Dilution of the warmed filtrate with ether yielded 0.035 gm. of diacetoxytrinitrotriazaheptane.

When equimolar quantities of methylene-bis-dinitrotriazacyclohexane and benzoyl nitrate (7) in dry acetone at -5° C. were allowed to react for 30 min. a product melting at 115° to 136° C. was obtained, which could partially be purified to melting point 147° to 148° C. by wash with acetone. This has not been identified. Partial destruction of the evaporated filtrate by 70% nitric acid left a 33% yield (mole for mole) of RDX.

1,9-Diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane from Crude Hale Cyclonite

When the dry crude Hale product (wt. 356 gm., m.p. 200° to 203.5° C. with shrinkage at 194° C.) from 2 moles hexamine and 40 moles 99% nitric acid was refluxed with boiling absolute ethanol for eight hours, the suspended RDX which was then filtered off melted at 203° to 203.5° C. (shrinkage 200° C.). The ethanolic filtrate was fractionally evaporated, and the content alternately crystallized fractionally 20 times from ethanol, dioxane, toluene, carbon tetrachloride, and mixtures of these. There were thus separated impure Cyclonite, impure 3,5-dinitro-3,5-diaza-1-oxacyclohexane and 5 mgm. of pure 1,9-diethoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane, m.p. 166° to 167° C. (mixed melting point not lowered). This result should, of course be considered qualitatively.

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NITROLYSIS OF HEXAMETHYLENETETRAMINE

VI. RECOMBINATION OF FRAGMENTS DURING HEXAMETHYLENE-TETRAMINE NITROLYSIS IN ACETIC ANHYDRIDE¹

BY E. ARISTOFF, J. A. GRAHAM, R. H. MEEN, G. S. MYERS, AND
G. F. WRIGHT

Abstract

Alternative hypotheses can account for the yield of more than one equivalent of Cyclonite from hexamine when the Bachmann reagents, ammonium nitrate, nitric acid, and acetic anhydride are used. In the nitrolysis, evidence for a stepwise synthesis from unit fragments is presented as the enhanced yield when methylenedinitramine is added with paraform to ammonium nitrate and acetic anhydride according to the Schiessler-Ross method for Cyclonite synthesis. However, this evidence is discounted because the expected by-product, 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane is not found. Alternatively it is believed that the Bachmann reaction is actually a combination of the direct nitrolysis of hexamine with nitric acid, concurrent with a resynthesis of hexamine from the fragments produced by the nitrolysis. On this basis all by-products from the hexamethylenetetramine nitrolysis must be accounted as degradation products of hexamethylenetetramine and not capable of synthesis from unit fragments like formaldehyde, ammonia, and acetic acid. No exception has been found; the addition of acylamides to the Bachmann reaction mixture increases the yield of two by-products, 1-acyl-3,5-dinitro-1,3,5-triazacyclohexane and 1-acyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. It has been shown that these can be formed only from degradation products of hexamethylenetetramine such as 1,5-diaceto-3,7-endomethylene-1,3,5,7-tetrazacyclooctane and acetaminomethylhexamethylenetetramine nitrate.

When ammonium nitrate is used together with nitric acid for the nitrolysis of hexamine in acetic anhydride, yields of Cyclonite are obtained which are greater than might be expected if one mole of hexamine were converted to one mole of the explosive (2). This process therefore differs from the Hale method by which hexamine is nitrolyzed in nitric acid alone. Yields from the latter reaction are always less than 100% on the 1 : 1 molar basis (13). It also differs from the Ross-Schiessler process which employs formaldehyde and ammonium nitrate in acetic anhydride and gives yields of 50 to 60% on the formaldehyde basis (18). The name that Bachmann has applied to his method (The Combination Process) implies that it includes both the Hale and the Ross-Schiessler reactions.

According to this implication, hexamine first reacts with the nitric acid to form Cyclonite and fragments involving formaldehyde. These fragments have to recombine in some manner to provide a cyclic structure from which more Cyclonite can be formed. The recombination would, according to this reasoning, take place by the reaction through which Ross and Schiessler obtained Cyclonite.

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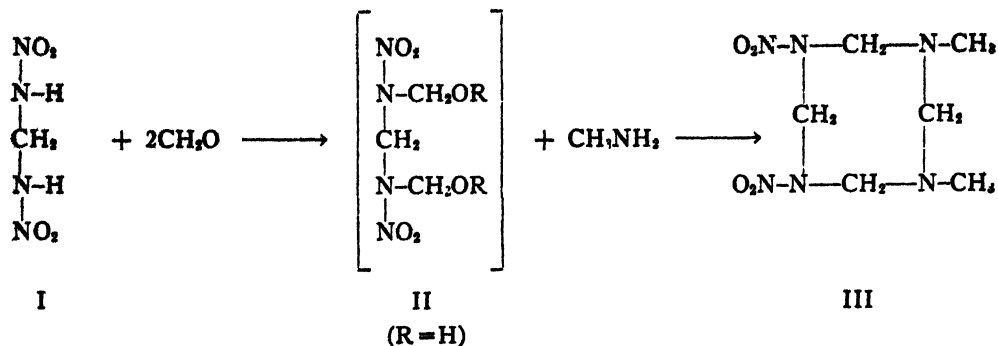
Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ontario.

In order to establish this scheme for Bachmann's synthesis, the method by which the Ross-Schiessler reagents combine must be known. There are two alternatives. Firstly, simple or polymeric methylenenitramine units might be formed and then cyclize to produce Cyclonite. In this event, the Hale nitrolysis might not be involved at all in the Bachmann process; the latter, too, could involve cyclization of methylenenitramine units. The second alternative would involve combination of the fragments of formaldehyde and ammonia to form hexamine (or a compound of similar complexity) which could then be degraded to Cyclonite by the path suggested for the Hale reaction (8, 16).

Either of these alternatives enjoys a certain amount of experimental evidence which seems to support it. Some of this evidence will be presented in the present report. It will be evaluated largely on the basis that any mechanism which is postulated must not only explain the formation of the principal product (Cyclonite) but also the by-products which are obtained at the same time. When the evidence presented thus far in this series, "Nitrolysis of Hexamine", has been so evaluated, it has indicated that neither Cyclonite nor a by-product has arisen in the nitrolysis medium by direct synthesis from smaller units but always by degradation of a larger unit.

The following experiment would indicate that Cyclonite can be formed from a linear methylenenitramine unit. The yield of Cyclonite in the Schiessler-Ross process is relatively low compared with that obtained by the Bachmann method, and maximum yields of 58 to 64% are the highest attainable by the former method. If in a Schiessler-Ross reaction mixture (1 mole of paraform, 1.25 moles of ammonium nitrate, and 10 moles of acetic anhydride) one includes one-fifth mole of methylenedinitramine, the crude Cyclonite yield is raised to 81% of theoretical. If two-fifths mole of methylenedinitramine is employed, the yield is increased to 87%. These yield increases cannot be owing to the formaldehyde which might be contributed by decomposition of the methylenedinitramine for several reasons. First, the amount contributed by decomposition would be insufficient in quantity. Second, a duplicate experiment wherein one-fifth mole of methylenedinitramine was used and the paraform was omitted gave a yield of only 10% of the Cyclonite which might be formed by this decomposition. A small amount of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane (17) (II, R = Ac) was obtained as well, showing that the decomposition did occur.

Although the discoverers (5) of methylenedinitramine, I, and others (22) had characterized it adequately, we sought further confirmation of the identity of the material which we prepared by their method. While its reaction with formaldehyde and ammonia produced no definite product, two substances were obtained with formaldehyde and methylamine.



According to analyses, one of these compounds ought to be the cyclic 1,3-dinitro-5,7-dimethyl-1,3,5,7-tetrazacycloöctane, III. The other could not be identified. Its insolubility in acetone indicates that it is either a polymer or a salt. Both substances were thermally unstable.

This reaction typifies a strong tendency toward methylation of methylenedinitramine. Although we were unsuccessful in attempts to isolate the dimethylol derivative of II (R=H) (22), this methylation could be demonstrated by digestion of methylenedinitramine with formaldehyde, sodium acetate, and acetic anhydride at 95° C. A 9% yield of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II (R=Ac), was obtained in addition to considerable amorphous polymeric material. One may assume, therefore, that 1,3-dihydroxy-2,4-dinitro-2,4-diazapentane, II (R=H), is reasonably stable in hot acetic anhydride.

The stability of II (R=Ac) was demonstrated by treating it with 98% nitric acid. A 22% yield of 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane, II (R=NO₂), was obtained in this way and identified with that prepared from 3,5-dinitro-3,5-diaza-1-oxacyclohexane (17).

Although it can thus be shown that methylenedinitramine will enhance the yield in the Schiessler-Ross reaction, and also will methylolate in acidic media, it does not necessarily follow that it is an intermediate in the normal reaction carried out at 60° to 70° C. which yields over 50% of the theoretical amount of Cyclonite. Indeed there is evidence against its presence, since a careful search of the products of this reaction has failed to discover any 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II (R=Ac) (8). It will be recalled that this compound was isolated when methylenedinitramine deliberately was added to the otherwise normal Schiessler-Ross reaction.

On the other hand, II (R=Ac) can be isolated in 1.4% yield (ammonium nitrate basis) when the Schiessler-Ross reagents are stirred together at room temperature for 25 times the normal reaction period. The reaction could not, however, be considered normal since the Cyclonite yield was only about 5% of theoretical and much polymeric material was present. An 18% yield of 3,7-*endomethylene*-1,5-dinitro-1,3,5,7-tetrazacycloöctane (DPT) was obtained as well, thus indicating the presence of dimethylolnitramide (6).

The situation with regard to methylenedinitramine can be summarized by the observation that it can be formed in a Schiessler–Ross reaction mixture, but not under conditions which are favorable to Cyclonite formation. Its significance in support of a reaction mechanism involving the direct construction of Cyclonite from small methylenenitramine units is therefore questionable.

The enhancement of Cyclonite yield when methylenedinitramine is added to the Schiessler–Ross reagents cannot be questioned, but the action of this substance can be explained otherwise than by direct participation in the formation of Cyclonite. Its strong tendency toward methylation may have the effect of withholding formaldehyde from the direct reaction until it is needed. Formaldehyde which is withheld in this manner will be less available for side reactions. One of the principal side reactions which prevents high yield in the Schiessler–Ross reaction is acetylation. Methylene diacetate will not form Cyclonite with acetic anhydride and ammonium nitrate.* It is suggested that the methylenedinitramine may be effective in reducing the tendency toward methylene diacetate formation.

The alternative to a synthesis of Cyclonite from methylenenitramine units is a synthesis of hexamine from formaldehyde and ammonium nitrate as part of the main reaction in the Schiessler–Ross process or as a secondary reaction in the Bachmann process. The nitration, according to this mechanism, will occur in the same manner as it does in the Hale process. Such a mechanism is inherently reasonable. Thus Baur and Ruetschi have shown that hexamine can be formed in acidic media (3) and Williams and Winkler have isolated it from formaldehyde and ammonium nitrate in acetic acid solution (21). Unfortunately hexamine reacts with acetic anhydride, so that these latter workers were unable to show its presence in a medium comparable with that employed by the Bachmann or Schiessler–Ross procedures, although they have postulated that its formation is necessary for Cyclonite formation in the latter procedure.

Direct proof is therefore lacking for a mechanism involving hexamine synthesis or resynthesis in these two anhydride processes. The indirect method which has been used successfully in this series, "Nitrolysis of Hexamine", has involved the isolation and identification of by-products, followed by a demonstration that they cannot be built up from smaller nitramine units, but must, instead, have been formed by degradation of hexamine. The remainder of this report will show that the by-products 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, and 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, always occur together in every Bachmann and Schiessler–Ross reaction; further that they must have been formed by degradation of hexamine.

The ordinary reaction mixture contains about 3% of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, and about 1% of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, on the basis that one mole of each is derived from one

* We are indebted to Dr. Paul Olynik for an investigation which showed that no Cyclonite could be isolated in a preparation where methylenediacetate was used instead of paraform in the Schiessler–Ross reaction.

mole of hexamine. Both are obtained by neutralization of the reaction liquors after the main product, Cyclonite, is filtered off (8). They have been identified by quantitative elemental, ammonia, and formaldehyde analyses and by qualitative detection of acetic acid from the products of decomposition. They have been converted by absolute nitric acid into 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, HMX, and Cyclonite, RDX, respectively.

The yields of both of these compounds can be increased (to 7.5% of the cyclooctane derivative VI) by use of a large excess of acetic anhydride in the Bachmann procedure (20). This suggests that the excess reacts with one of the ingredients; the nature of the by-product would indicate that acetamide is involved. Since both ammonium acetate and ammonium nitrate are present in the Bachmann reaction mixture, the action of acetic anhydride on each of these salts has been examined.

An 83% yield of acetamide was obtained when ammonium acetate was heated with the anhydride for a short time. The reaction with ammonium nitrate was much slower, but a yield of 7% of acetamide could be isolated; twice as much probably was present. When nitric acid was added to either of these reaction mixtures, no acetamide was formed.

Since nitric acid inhibits acetamide formation and yet is necessary for the subsequent nitrolysis there ought to be an optimum nitric acid - ammonium nitrate ratio for maximum yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, if its formation involves acetamide. Table I shows that this is the case when an excess of acetic anhydride is used over that required by Equation I.



and the ratio HNO_3/NH_4NO_3 is varied from 2 (as required by this equation) between the limits 1.5 and 2.5.

TABLE I

YIELD OF 1-ACETO-3,5,7-TRINITRO-1,3,5,7-TETRAZACYCLOOCTANE FROM BACHMANN TYPE REACTION USING 0.05 MOLE HEXAMINE AND 0.6 MOLE ACETIC ANHYDRIDE

Moles HNO_3 Moles NH_4NO_3	2.4	2.2	2.1	2.0	1.9	1.8	1.7	1.6	1.5
Yield, mgm.	20	23	1.5	145	400	460	310	230	200

If acetamide were necessary for the ultimate formation of acetotrinitro-tetrazacyclooctane, VI, and acetodinitrotriazacyclohexane, X, then deliberate addition of such an acid amide to the reaction mixture ought to increase the yield of these aceto compounds. This was found to be the case when 1 mole each of acetamide and hexamine in acetic acid were added to 9 moles of acetic anhydride proportionately with a solution of 4 moles of nitric acid and 2.5 moles of ammonium nitrate. The presence of the acetamide not only lowered the yield of Cyclonite to 58% but it also caused the formation of at least 8.5%

of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, and 3.5% of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, expected if one mole of each was formed from one mole of hexamine.

One might question the significance of this acetamide addition in a medium consisting largely of acetic acid and anhydride. The significance was verified by use of propionamide rather than acetamide. After removal of a 39% yield of Cyclonite, the neutralized liquors precipitated an 8.5% yield of 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane. This compound was adequately identified by quantitative elemental analysis and by qualitative identification of the propanoic acid produced by its decomposition in sulphuric acid. Also the compound was converted by absolute nitric acid to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. It would seem, therefore, that the acid amide was a significant constituent, at least so far as the tetrazacyclooctane was concerned. We failed, however, in the synthesis of the corresponding benzoyl derivative when we included benzamide with the reagents used in the Bachmann process. A good yield of methylene-*bis*-benzamide was obtained instead.

It should not be implied that the acid amides were replacing ammonium nitrate in the process. Evidence that they were *supplementing* the nitrate salt was furnished by several experiments. When half the ammonium nitrate required by Equation I was replaced by acetamide the Cyclonite yield was reduced to 41% (2 : 1 basis) and the acetotrinitrotetrazacyclooctane yield to 5.3%. When all of the ammonium nitrate was replaced by acetamide only 22% of Cyclonite was obtained and none of the aceto compound, VI, could be detected. A 19% yield (1 : 1 basis) of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane appeared instead.

By analogy with the postulated formation of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and Cyclonite (15, 16) one might expect that the aceto compounds found as by-products in the processes involving acetic anhydride would result from substances comprising acetamide, formaldehyde, and ammonia. Two known compounds appeared as possibilities since they both seemed to contain acetamino linkages. The first of these was a compound prepared by the action of one equivalent each of nitric acid and acetic anhydride on hexamine (14) and later designated as the quaternary salt (1) 1-acetamidomethylhexamine-1-nitrate, IV, by Bachmann and coworkers. The other possibility was a compound prepared from hexamine and acetic anhydride alone (10) by Dominikiewicz who specified it as diacetylpentamethylenetetramine. Neither compound was reported as preparable from acetamide, formaldehyde, and ammonia, and all attempts by us to prepare either from these reagents in acetic anhydride or acetic acid failed completely. It thus appeared that if these compounds turned out to be responsible for acetotrinitrotetrazacyclooctane, VI, and acetodinitrotriazacyclohexane, X, then they must have been secondary alterations of the true resynthesis product, hexamine.

When the first-mentioned of the two compounds, so-called 1-acetamidomethylhexamine-1 nitrate was treated with the Bachmann reagents at 65° C.

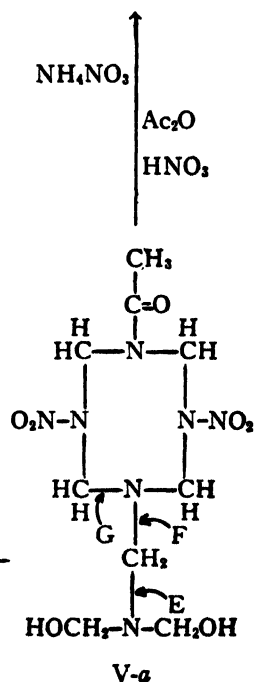
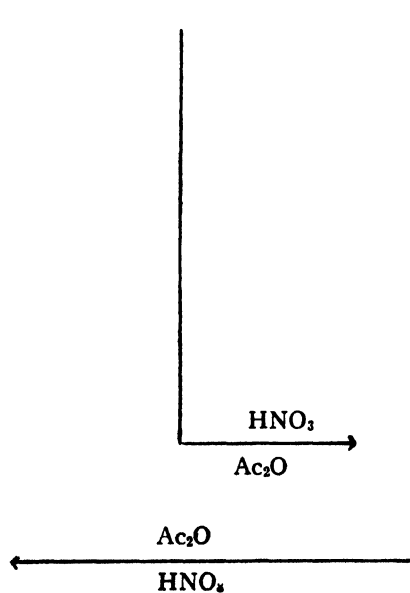
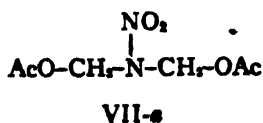
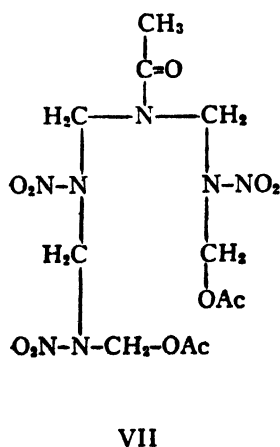
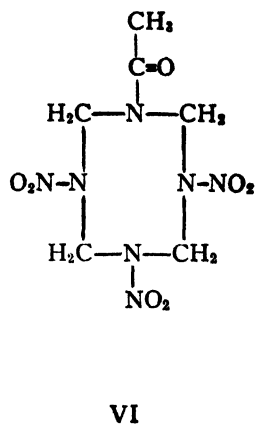
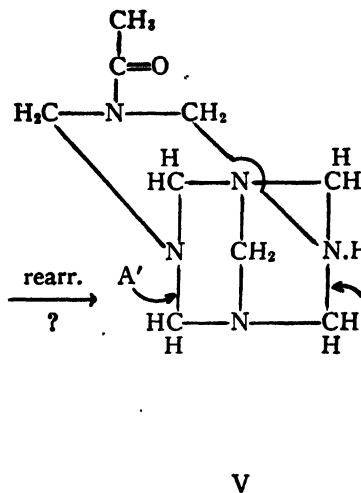
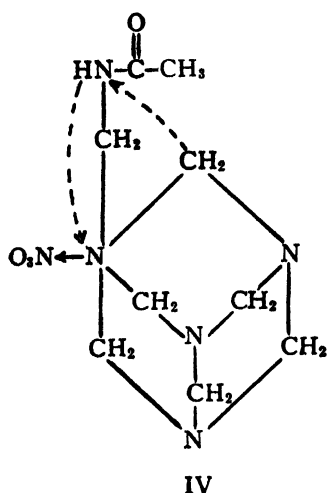
a 17% yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, was formed together with a 40% yield of a mixture of Cyclonite and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. A rigorous search, however, revealed no isolable amount of the 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X. It would seem then that both of the aceto compounds X and VI were not formed from the same source.

The structure of 1-acetamidomethylhexamine-1 nitrate has been well established (1). We found further confirmation in its inertness toward diazomethane, since hexamine mononitrate was easily converted to hexamine methonitrate by this reagent. Although the evidence for a quaternary salt structure is thus convincing, it is difficult to explain the formation of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, from such a structure. On the other hand, if VI were derived from 1,5-*endomethylene*-3,7-[*endodimethylene*-N-acetamido]-1,3,5,7-tetrazacyclooctane, V, then this latter ternary salt could be considered as a rearrangement product in which a 1,3-shift of methylene was compensated by a 1,3-shift of hydrogen within the quaternary ion, IV. It is interesting to note that the multiple 1,3-shift must occur in this case in the same manner as do all 1,2-rearrangements, i.e., with inversion from tetrahedral apex to base. The rearrangement is illustrated by the dotted arrows in IV.

Under any circumstances V represents a reasonable structure from which VI can be derived by nitrolysis without any concurrent production of acetodinitrotriazacyclohexane, X. Thus by complete analogy with the nitrolysis of hexamine (16) the initial scission can be specified at A,A' in V. If esterification is hindered in V-a (by presence of ammonium nitrate) then demethylolation can occur until linkage F is reached, after which nitration will give acetotrinitrotetrazacyclooctane, VI. If esterification is possible in V-a (absence of ammonium nitrate) then scission with esterification will occur at E and subsequently at G. This would account for the reaction product 1,9-diacetoxy-6-aceto-2,4,8-trinitro-2,4,6,8-tetrazanonane, VII, which was isolated by Carmack and associates when they treated IV (or hexamine) with nitric acid and acetic anhydride (9). We have repeated their preparation to obtain a 51% yield of VII from IV and also a 36% yield of the other fragment, diacetoxydimethylnitramine, VII-a.

The enhancement in yield of IV from hexamine, nitric acid, and acetic anhydride when acetamide is included with these reagents (1) strongly recommends V as the intermediate from which acetotrinitrotetrazacyclooctane, VI, is formed in the Bachmann reaction, since the yield of VI is likewise increased when acetamide is added to the Bachmann ingredients. Earlier in the present report it has been shown that the effect of this included acylamide was independent of the anhydride. The relationship of this effect to the formation *in situ* of IV was obtained by treating a homologue of IV, propanoylamidomethylhexamine-1 nitrate (1), with acetic anhydride, ammonium nitrate, and nitric acid under Bachmann reaction conditions; then alternatively IV was treated with propionic anhydride, ammonium nitrate, and nitric acid. In

addition to Cyclonite and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane there were obtained from the two reactions specifically 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, and 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, respectively. Neither product was contaminated with the other.



Although 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, could not be obtained from the compound that Bachmann and coworkers designated as IV, it was found that a 3 to 5% yield of X could be obtained, in addition to Cyclonite, when 3,7-*endomethylene*-1,5-diaceto-1,3,5,7-tetrazacyclooctane, VIII (10), was nitrolyzed under conditions of the Bachmann reaction. The actual yield was probably higher than the 3 to 5% which was isolated, since contamination with unidentified impurities made the separation difficult. However, this difficulty would not invalidate our assurance that none of the acetotrinitrotetrazacyclooctane, VI, was present in this reaction mixture. None of VI would be expected if VIII has the structure assigned to it. This assigned structure explains, by nitrolysis at G and G', the formation of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X.

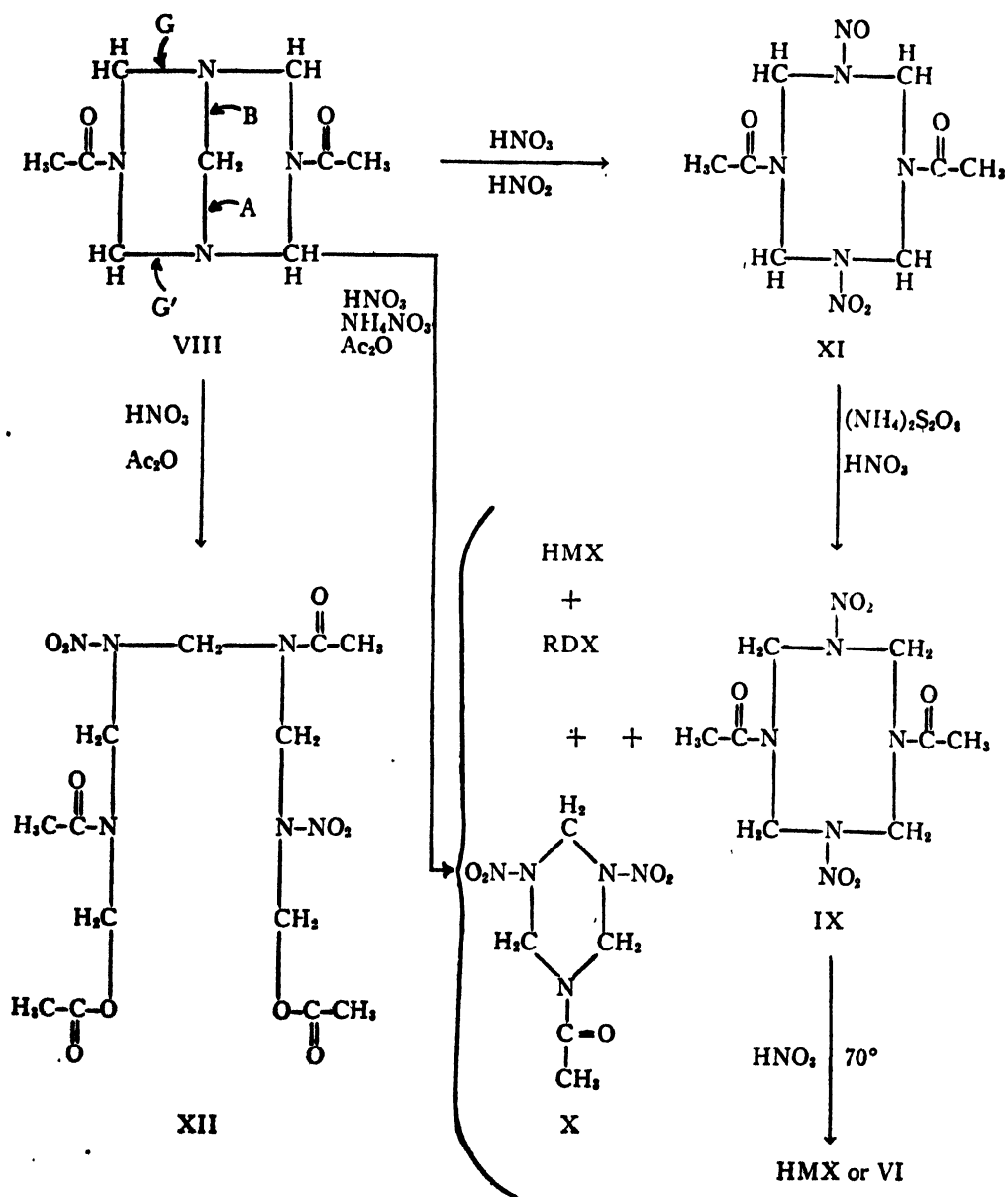
Instead of VI a high melting compound was found in 4 to 7% yield. Its empirical formula was $C_6H_{14}N_6O_8$. Since this compound possessed the same solubility characteristics as 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) it was difficult to free it from this contaminant. The compound was finally obtained in a state of purity by the following alternative method of preparation: the oxidation of 1,5-diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI, by ammonium persulphate (7) in nitric acid yielded the same high melting compound in 77% yield. Since 1,5-diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI, had also been prepared from 3,7-*endomethylene*-1,5-diaceto-1,3,5,7-tetrazacyclooctane (12), VIII, this established the structure of the new compound as 1,5-diaceto-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IX.* Its mode of formation from VIII is evident (by analogy with the formation of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (6)) as scission at A in structure VIII followed by demethylolation and nitrolysis at B. Finally IX was characterized by its conversion to 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, or to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), depending on the temperature at which the nitration was carried out. Carmack and his coworkers prepared, in small yield from 3,7-*endomethylene* 1,5-dinitro-1,3,5,7-tetrazacyclooctane and acetic anhydride, a compound melting at 257° C. (4). We have purified their compound rigorously and find it to be identical with IX.

This intercorrelation among related structures was established in another way. It has been found (1, 15) that elimination of ammonium nitrate from the set of Bachmann reagents induces alternative scission of the cyclic structures of the hexamine type. Thus 3,7-*endomethylene*-1,5-dinitro-1,3,5,7-tetrazacyclooctane (DPT) reacts with nitric acid and acetic anhydride to give the linear polymethylenenitramine 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (15). When 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane, VIII, was treated with these reagents a compound was obtained which ought, on the basis of its elemental analysis, to be 1,9-diacetoxy-2,6-diaceto-4,8-dinitro-2,4,6,8-tetrazanonane, XII. This would be the

* It also confirmed, by intercorrelation, the structure for VIII for which the nitrogen analyses were never entirely satisfactory until Kjeldahl rather than Dumas analyses were carried out.

expected compound if nitrolysis and esterification occurred at A in structure VIII; then subsequently at G.

We have thus shown that the aceto compounds VI and X can be prepared under the conditions of the Bachmann reaction from the two progenitors, IV (or V) and VIII, which in turn have, up to the present, only been prepared from hexamine. While one of the two aceto compounds, 1-aceto-3,5-dinitro-1,3,5-triazahexane has been prepared by acetylation of 3,5-dinitro-3,5-diazapiperidinium nitrate (19), no comparable synthesis of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, exists. It is reasonable to assume that both



compounds are formed in the same manner since they always exist together. The preponderance of evidence with respect to these aceto compounds, as well as with the other by-products and main products of the Bachmann and Schiessler-Ross reaction, is in favor of their synthesis by selective nitrolytic and acetolytic degradation of hexamine rather than by stepwise synthesis from its fragments. The Schiessler-Ross reaction may then be considered as the secondary phase of the Bachmann reaction. On this basis the Schiessler-Ross reaction comprises a synthesis of hexamine from formaldehyde and ammonium nitrate together with a nitrolysis of the Hale type by the nitric acid which thus is set free according to Equation II.



In conclusion it should be pointed out that the mechanism of formation of one by-product of hexamine nitrolysis has never been satisfactorily explained. This compound, 3,5-dinitro-3,5-diaza-1-oxacyclohexane (17), has never been synthesized from simpler substances nor produced by degradation of any substance except hexamine. It may be significant that it never is encountered under conditions to which one can refer as those of Bachmann or of Schiessler and Ross but only those of Hale. Until the genesis of this compound is satisfactorily explained, however, one cannot consider the nitrolysis of hexamine as completely elucidated.

Experimental*

Nitrolysis of Hexamine with the Schiessler-Ross Reagents at 25° C.

Finely ground ammonium nitrate, 32 gm. (0.4 mole) and 18 gm. (0.6 mole) of Roessler and Hasslacher paraform were added to 21 cc. (0.37 mole) of acetic acid and 95 cc. (1 mole) of acetic anhydride. This suspension was stirred for 19 hr. at 25° C., then diluted with a solution of 300 cc. water and 10 cc. of 70% nitric acid at 60° C. This was stirred for 15 min. at 35° C., cooled to 0° C. and filtered to remove 4.77 gm. An aliquot of this sticky precipitate was found by hot digestion with 70% nitric acid to contain 32% of its weight as crude Cyclonite, m.p. 189° to 190° C. This represents a yield 5.2% of theoretical on the ammonium nitrate basis. The Cyclonite was separated by hot methanol extraction to leave an insoluble amorphous residue with elemental analysis conforming to $\text{C}_7\text{H}_{15}\text{N}_8\text{O}_{11}$. It was insoluble in alkali, acid, ethanol, nitromethane, acetic acid, benzene, and dioxane but could be separated by boiling acetic anhydride into 30% of material melting at 232° to 233.5° C. (decomp.) with elemental composition conforming with $\text{C}_8\text{H}_6\text{N}_3\text{O}_4$ and 70% which decomposed without melting at 281° to 296° C. The elemental analysis of this latter material conformed with $\text{C}_{11}\text{H}_{24}\text{N}_{16}\text{O}_{18}$. A large amount of formaldehyde was lost during the separation with acetic anhydride.

The acidic aqueous filtrate from which the crude precipitate had been removed was neutralized to pH 6 with 28% ammonia. The sticky solid which precipitated weighed 5.56 gm. It was separated by 25 cc. of warm ethanol

* All melting points have been corrected against reliable standards.

into 3.86 gm. of insoluble material melting at 195° to 196° C. (decomp.). This represents an 18% yield (ammonium nitrate basis) of 1,5-dinitro-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane since its mixed melting point with this substance was not lowered. The alcoholic solution was cooled and evaporated to yield 0.77 gm. of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, II, (R=Ac), or 1.4% of theoretical (ammonium nitrate basis). This was purified to melt at 104° to 105° C. by crystallization from ethanol. The mixed melting point with authentic material was not lowered.

Methylene Diacetate in the Schiessler-Ross Reaction

In order to avoid an induction period in this test reaction, a normal 0.1 molar (18) reaction was carried out. With the temperature still maintained at 69° to 70° C. a solution of 0.1 mole methylene diacetate (n_D^{24} 1.4125), 0.1 mole acetic acid, and 0.26 mole of acetic anhydride was added over a 20 min. period while five 1.60 gm. portions of ammonium nitrate were introduced over the same time. There was no characteristic heat evolution during this addition. Subsequent processing gave Cyclonite in yield of 47% on the basis of the paraform used in the initial step. The methylene diacetate thus does not contribute to Cyclonite formation.

1,3-Dinitro-5,7-dimethyl-1,3,5,7-tetrazacyclooctane, III.

A solution of 1.36 gm. (0.01 mole) of methylenedinitramine (5) in 4.5 cc. (0.06 mole) of 40% formalin was allowed to stand at 25° C. for 10 min. It was then cooled to 0° C. and treated with 2.1 cc. (0.02 mole) of 30% aqueous methylamine. The precipitate, which separated immediately, was filtered after the reaction mixture had aged for 20 min. more at 0° C. This product weighed 1.13 gm. and melted at 91° to 93° C. (decomp.). It was extracted with 8 ml. of absolute ethanol at 25° C. to yield a solution which was evaporated to dryness in an air stream. The residue weighed 0.04 gm. and melted at 108° C. (decomp.). This thermally unstable compound was analyzed without further purification. Its yield was further augmented to about 25% of theoretical by further ethanol and acetone extraction of the residue. Calc. for $C_8H_{14}N_6O_4$: C, 30.7; H, 6.04; N, 35.8%. Found: C, 31.1; H, 6.13; N, 35.3%. The residue from the ethanol extraction was further washed with ethanol and acetone until the melting point could not be raised above 134° to 135° C. The remainder weighed 0.75 gm. The structure of this compound has not been ascertained. Calc. for $C_8H_{14}N_8O_{10}$: C, 19.4; H, 3.77; N, 33.8%. Found: C, 19.4; H, 3.79; N, 34.3%.

Methylenedinitramine with Formaldehyde

Methylenedinitramine, 0.22 gm. (0.0016 mole), was dissolved in 0.24 cc. (0.0032 mole) of 40% formalin at 0° C. and one drop of pyridine was added. A solid settled out over a period of two or three days at 0° C. and after nine days the amorphous material was filtered, ground up with 25 cc. of water, and dried at 50° C. Weight of the product was 0.19 gm.; decomposition range was 219° to 230° C. (brown residue). Yield is 86% by weight on the methylenedinitramine. A portion, 0.16 gm., of this product was suspended in 10 cc.

of acetone at 25° C. and the residue (0.11 gm.) was extracted with 6 cc. of boiling ethanol and two 5 cc. portions of boiling acetone. The residue which remained decomposed to a brown residue over a range of 216° to 228° C. and was found to have the following analysis. Calc. for $C_6H_{12}N_9O_{10}$: C, 16.7; H, 3.36; N, 35.2%. Found: C, 16.4; H, 3.257; N, 34.8%.

This product was completely destroyed in boiling 70% nitric acid, indicating the absence of RDX. It is insoluble in boiling acetone, ethanol, benzene, and nitromethane. It is somewhat soluble on standing in 99% nitric acid at 25° C. and is recovered on dilution with water in yields of 70% to 80%. It is evidently a methylenedinitramine-formaldehyde polymer.

Addition of Methylenedinitramine to the Schiessler-Ross Reagents

A finely ground mixture of 10 gm. of ammonium nitrate (0.125 mole), 3 gm. (0.1 mole) of Roessler and Hasslacher paraform and also 2.72 gm. (0.02 mole) of methylenedinitramine, m.p. 101° C., were added equivalently and proportionately with stirring to a solution of 5.7 cc. (0.1 mole) of acetic acid in 25 cc. (0.26 mole) of acetic anhydride at 70° C. over a period of 14 min. The reaction mixture was stirred 30 min. longer at 70° C. and then cooled to 0° C. and the precipitate filtered and water-washed. Weight of the product was 6.0 gm., m.p. 190° to 196° C. (shrinkage 189° C.). Yield calculated as crude Cyclonite is 81.2% of theory (formaldehyde basis). This crude product was found to contain 92% Cyclonite-HMX by "fume off" with 70% nitric acid, m.p. 196° to 202° C. The filtrate was neutralized to pH 6 with 28% ammonia and no precipitate of DPT was obtained. If the methylenedinitramine had not been added to this otherwise normal Schiessler-Ross reaction mixture, the yield of crude Cyclonite would have been 58%. The following procedure describes the behavior when methylenedinitramine is used and the paraform is omitted.

To a solution of 2.9 cc. (0.05 mole) of acetic acid in 12.5 cc. (0.12 mole) of acetic anhydride which was warmed to 70° C. was added with stirring a mixture of 5.0 gm. (0.063 mole) of ammonium nitrate and 2.72 gm. (0.02 mole) of methylenedinitramine over a period of 14 min. at $70 \pm 1^\circ$ C. The reaction mixture was stirred 90 min. longer at 70° C. and then diluted with 50 cc. of water, cooled to 20° C., and the precipitate filtered. Weight was 80 mgm., m.p. 200° to 202° C. The filtrate was neutralized to pH 6 with 28% ammonia and allowed to stand at 0° C. for two hours. The precipitate which settled out was filtered, water-washed, and dried at 50° C. Weight was 0.11 gm., m.p. 161° to 182° C. This was separated by crystallizations from ethanol into 65 mgm. of Cyclonite, m.p. 194° to 197° C. and 12 mgm. of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, m.p. 95° to 97° C. The total yield of Cyclonite is then 0.145 gm. (9.7% of theoretic, methylene basis). The yield of crude 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane is 0.65% of theory (methylene basis).

Preparation of 1,5-Diacetoxy-2,4-dinitro-2,4-diazapentane

To a solution of 2.72 gm. (0.02 mole) of methylenedinitramine in 3 cc. (0.04 mole) of 40% formalin at 25° C. was added 3.28 gm. (0.04 mole) of anhydrous sodium acetate and 20 cc. (0.2 mole) of acetic anhydride. The resulting mixture was warmed to 95° C. for one hour, drowned in 85 cc. of ice-water mixture and neutralized to pH 6 with 28% ammonia. The flocculent precipitate was filtered after standing overnight at 0° C., water-washed, and dried at 50° C. Weight of product was 2.15 gm. The material did not seem to melt or decompose below 275° C. This product was separated by crystallizations from acetone and ethanol into a 9% yield of 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane, m.p. 90° to 92° C., (1 : 1 molar basis) and 1.15 gm. of acetone insoluble compound which decomposed to a brown solid residue over a range of 280° to 315° C. It burst into flame on being heated on a hot spatula and burned like cordite. It could not be detonated by striking on the anvil with a hammer. The material was insoluble in 5 *N* nitric acid and gave a negative test for sodium. It was purified by extraction with boiling acetic anhydride and analyzed. Calc. for $C_{11}H_{24}N_8O_{10}$: C, 21.3; H, 3.86; N, 33.7%. Found: C, 21.2; H, 3.84; N, 33.4%.

Attempted Synthesis of 3,5-Dinitro-3,5-diaza-1-oxacyclohexane (17)

A solution of 0.68 gm. (0.005 mole) of methylenedinitramine in 0.9 cc. (0.012 mole) of 40% formalin was added rapidly to 22.4 cc. (0.5 mole) of 95% nitric acid which had been cooled to 0° C. The solution was allowed to stand in an ice-bath for 40 min. and then drowned in 40 cc. of ice-water mixture. The precipitate which settled out was washed acid-free with water and dried over phosphorus pentoxide *in vacuo*. Weight was 0.31 gm., m.p. 112° to 115° C. (decomp.). Yield calculated as 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane is 22% of theory (methylenedinitramine basis). This material was identified as 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane by mixed fusion with an authentic sample and also by its conversion to the dimethoxy derivative on treatment with boiling methanol. The drowned acid filtrate from this reaction was neutralized to pH 6.5 with 28% ammonia and then extracted with chloroform. The chloroform extracts were found to contain no 3,5-dinitro-3,5-diaza-1-oxacyclohexane.

Other attempts to prepare this compound by treating both 1,5-dinitroxy-2,4-dinitro-2,4-diazapentane and 3,5-dinitro-3,5-diazapiperidinium nitrate with 92% and 95% nitric acid failed to give the desired product. We were likewise not able to dehydrate a solution of 1 mole of methylenedinitramine in 2 moles of 40% formalin to 3,5-dinitro-3,5-diaza-1-oxacyclohexane by vacuum evaporation at 60° to 100° C. over a four hour period.

1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI

A solution 33.6 gm. (0.24 mole) of hexamine in 160 cc. (2.8 moles) of acetic acid was added simultaneously, equivalently, and continuously with a solution of 38.4 gm. (0.48 mole) of ammonium nitrate in 46.5 cc. (1.1 moles) of 99% nitric acid into 640 cc. (6.18 moles) of well stirred acetic

anhydride at 65° C. The temperature during the 20 min. addition period was held at 69° ± 2° C. The solution was aged 20 min. longer at 65° ± 2° C. and then diluted slowly with 1200 cc. of water, cooled to 20° C., and was filtered. The yield of crude Cyclonite was 52.8 gm., m.p. 192° to 198° C. (soft 189° C.) or 50% on the formaldehyde basis.

The filtrate was neutralized to pH 5.6 with 28% ammonia. After five days at 2° C., 9.1 gm. of solid, m.p. 181° to 194° C. (soft 175° C.), settled out. This crude VI was suspended in 30 cc. of acetone and boiled for a few minutes. The insoluble residue melted at 213° to 214° C. (wt. 2.31 gm.) while the solution on cooling yielded 3.0 gm., m.p. 215° to 217° C. The total crude yield of 5.3 gm. was 7.5% on the hexamine basis.

The crude compound was crystallized several times from acetone and nitromethane to melt at 224.2° to 224.7° C. with frothing. The compound is slightly soluble in pyridine, acetone, and nitromethane, but almost insoluble in ethanol, benzene, acetic acid, and ether. It is destroyed readily by hot 70% nitric acid and warm 10% aqueous sodium hydroxide. It decomposes slowly in 28% ammonia. It can be detonated by a hammer blow on the anvil. Calc. for $C_6H_{11}N_7O_7$: C, 24.6; H, 3.76; N, 33.4%. Found: C, 24.9; H, 3.75; N, 33.6%.

A positive test for acetate could be obtained by decomposing 1 gm. of VI in 10 cc. of 96% sulphuric acid at 20° C. After frothing had ceased, the solution was cooled, diluted with 6 cc. of water, refluxed 15 min. and then distilled. The distillate, which gave a positive lanthanum nitrate test for acetic acid (11), was titrated with 0.1 *N* aqueous sodium hydroxide using phenolphthalein to indicate 92% of the acetyl expected if VI contains one acetyl group. The neutralized solution was evaporated and treated with *p*-bromophenacyl bromide to yield the identifying acetate.

The acetic acid was identified also through the reaction of VI with 98% nitric acid. A 25% yield of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane could be isolated (m.p. 278° C.) by treatment at 5° C. (subsequently at 55° C.) with 33 equivalents of 98% nitric acid. After this compound was filtered from the alkali-neutralized liquor, the filtrate was boiled under reflux with 276 gm. of ferrous sulphate and an excess of sulphuric acid until the brown fume ceased to be evolved. The acetic acid was finally distilled off in quantity and identity as outlined above.

1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane, X

When the neutralized filtrate from which VI is filtered was allowed to stand for 19 days, a further 2.45 gm. of material was precipitated. When this was combined with the evaporated mother liquors from which VI was crystallized, then ground and centrifuged in an ethylene dibromide – petroleum ether mixture of density 1.71, a layer less dense than this medium could be separated from the top. The 1.8 gm. (m.p. 136° to 138° C.) so obtained was repeatedly crystallized from ethanol and 1 : 1 ethanol : acetone to melt at 158° C.

Calc. for $C_6H_9N_5O_5$: C, 27.4; H, 4.14; N, 31.9; CH_3COO , 19.6%. Found: C, 27.4; H, 4.14; N, 31.9; CH_3COO , 19.1%.

The molecular weight was first determined reproducibly by the micro-Rast method in camphor as 262, but later it was found that if the camphor solution of X were heated for 10 to 15 min., another reproducible value of 220 (calculated for $C_6H_9N_5O_5$, 219) was obtained. This behavior is undoubtedly owing to incompleteness of apparent solution and seems to be characteristic of many cyclic nitramines.

When 1 gm. of X was boiled 17 hr. with 50 cc. of *N*/2 sulphuric acid (solution after 15 min.), analysis for formaldehyde by the dimedone method and for ammonia by the Kjeldahl method gave values of 39.3% CH_2O and 8.9% NH_3 (calc. for $C_6H_9N_5O_5$: CH_2O , 41.1; NH_3 , 7.8%). Decomposition of X in 96% sulphuric acid with subsequent dilution and distillation gave Duclaux numbers characteristic for acetic acid. Identification was also effected by the *p*-bromophenacyl ester.

When 0.5 gm. of X was added to 5.9 cc. of 99% nitric acid at 65°C. and digested at this temperature over a 30 min. period, dilution gave 0.25 gm. of a crude product, m.p. 178° to 194° C., from which a 38% yield of Cyclonite m.p. 201° to 204° C. was obtained after digestion with hot 70% nitric acid.

Compound X could also be prepared from 3,5-dinitro-3,5-diazapiperidinium nitrate (19). Cyclonite (19) is the main product when the amine nitrate is heated in acetic anhydride alone. The addition of 0.41 gm. (0.005 mole) of sodium acetate to 3 cc. (0.053 mole) of acetic acid and 6.0 cc. (0.06 mole) of acetic anhydride, on the other hand, gave a solution which was stirred at 25° C. for nine hours with 1.2 gm. (0.005 mole) of the dinitrodiazapiperidinium nitrate. This reaction mixture, when diluted into 50 cc. of ice and water and neutralized with 28% ammonia to pH 5.6, gave 0.51 gm. of precipitate after four hours at 2° C. This melted at 151° to 153° C. when water-washed and dried at 95° C. Purification of this 46% yield in boiling ethanol raised the melting point to 156° C. (if the amine nitrate, m.p. 99° to 100° C. was free from Cyclonite), and it could thus be identified by mixed melting point.

A third method of preparation of X has been described previously (8) from methylene-*bis*-1-[3,5-dinitro-1,3,5-triazacyclohexane].

Addition of Acetamide to Bachmann Reagents

A solution of 2.52 moles of ammonium nitrate in 4.06 moles of 99% nitric acid and a solution of 1 mole of hexamine and 1 mole of acetamide in 11.65 moles of acetic acid was added proportionately over 45 min. from two burettes to 9.3 moles of stirred acetic anhydride at 65° C. The yield of crude Cyclonite, m.p. 178° to 180° C. (which separated after the mixture was heated 10 additional minutes, then diluted fivefold with water and let stand at 0° C. overnight was 58.3% of theoretical.

A suspension of 20 gm. of this product in 20 cc. of acetone was filtered and washed slowly with five 10 cc. portions of the same solvent. There remained 14.1 gm. of Cyclonite, m.p. 197° to 198° C. (soft at 188° C.). The filtrate was

evaporated to yield 0.62 gm. of material, m.p. 221°C . After crystallization from nitromethane it melted at 223°C . and did not depress the melting point of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI.

Further concentration of the acetone solution yielded 1.80 gm. which on crystallization from nitromethane turned out to be 30% of VI and 70% of Cyclonite plus 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, HMX. The remaining mother liquors were evaporated and the residue fractionally crystallized from 1 : 1 ethanol-acetone to yield 0.25 gm. of impure VI, m.p. 214° to 215°C . and 1.78 gm. having approximately the composition of the original mixture. The remainder of the mother liquor yielded 0.69 gm. of impure 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, melting at 140° to 160°C . from which the pure compound, m.p. 158°C ., was isolated by ethanol crystallization and identified by mixed melting point.

Since 1.78 gm. of the fractionally crystallized material can be considered as not separated, the distribution of the remaining 18.22 gm. may be estimated as follows:

Cyclonite plus tetranitrotetrazacyclooctane	15.70
1-Aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI	1.47
1-Aceto-3,5-dinitro-1,3,5-triazacyclohexane, X	0.69
Unaccounted	0.36

These quantities represent 8.5% and 3.5% yields (1 : 1 basis) of VI and X respectively.

Effect of Ammonium Nitrate-Nitric Acid Ratio on Yield of VI

In a typical preparation of Cyclonite by the Bachmann procedure, 160 cc. (1.70 moles) of acetic anhydride was charged into the stirred reaction flask and the temperature raised to 68°C . Thereupon, 48.5 gm. (0.606 mole) ammonium nitrate previously dissolved in 41 cc. (0.975 mole) of 98% HNO_3 and 33.6 gm. (0.24 mole) of hexamine dissolved in 160 cc. (2.8 moles) of acetic acid were measured proportionately from the burettes with the nitric acid solution leading by 5% (vol.). When the water bath was lowered approximately to 45°C ., the temperature of the reaction could be regulated conveniently between 65° and 70°C . by controlling the rate of addition. Under these circumstances, between 15 and 20 min. was usually required to complete the addition. The reaction mixture was then heated to 90°C . with stirring before dilution with 400 cc. of hot water. The first 15 cc. of water was added slowly to determine whether any free anhydride remained. The diluted solution was then simmered at 90°C . for at least one-half hour; during this period considerable gassing could be observed if the stirring were stopped. After pouring in an additional 250 cc. water, the mixture was cooled to 0°C . usually overnight. After suction filtration, the product was washed neutral to bromocresol green with about one liter of water and dried by air draft.

The 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane, HMX, in this crude Cyclonite was determined on a sample obtained by evaporation of an acetone solution followed by centrifugation of the ground residue in iodobenzene.

The tetranitro compound was more dense than 1.83, and therefore settled to the bottom of the tube.

The relative yield of VI was obtained by filtration of the diluted reaction filtrate aliquots after 30 days.

The variations in ammonium nitrate-nitric acid ratio are shown in Table II.

TABLE II

Moles HNO ₃	Moles NH ₄ NO ₃	Mole ratio HNO ₃ /NH ₄ NO ₃	Yield crude Cyclonite	% HMX in crude Cyclonite	Wt. yield of VI, mgm.
4.63	2.0	2.31	77	5	20
4.30	2.0	2.15	73	9	0
4.06	2.0	2.03	69	13	310
4.06	2.04	1.98	69	13	505
4.06	2.08	1.96	75	10	560
4.06	2.08	1.96	70	12	470
4.06	2.20	1.85	74	11	460
4.06	2.52	1.61	80	6	285
4.06	2.79	1.46	70	7	70

1-Propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane

The preparation involving added acid amide (outlined above) was repeated with the exception that propionamide was used instead of acetamide. After removal of a crude Cyclonite yield (m.p. 198° to 201° C.) of 39% the filtrate was neutralized to pH 5.6 with ammonia and evaporated under 11 mm. almost to dryness. The crystal residue was stirred with 500 cc. water and then filtered to remove material melting at 161° to 165° C. which contained 32% of Cyclonite according to the weight of residue obtained after oxidation with hot 70% nitric acid. The crude was crystallized from acetone and nitromethane to melt at 199° to 200° C. This new compound was produced in 8.5% yield on the basis that it was the only product except Cyclonite which was present in the crude material obtained by neutralization of the reaction liquor. Calc. for C₇H₁₃N₇O₇: C, 27.4; H, 4.24; N, 31.8; CH₂O, 39.1; NH₃, 5.54%. Found: C, 27.6; H, 4.24; N, 31.8; CH₂O, 36.3; NH₃, 5.82%. The compound, after decomposition with 96% sulphuric acid, gave Duclaux numbers expected for propionic acid, and *p*-bromophenacyl propionate was prepared from the neutralized Duclaux distillate. The compound could be converted in 26% yield to tetranitrotetrazacyclooctane (HMX) by treatment of 0.48 gm. (0.0016 mole) in 5.5 cc. (0.13 mole) of 98% nitric acid at 40° C. for 20 min., followed by dilution with water.

Addition of Benzamide to Bachmann Reagents

When one equivalent of benzamide was added in acetic acid solution proportionately to the other reactants in the Bachmann reaction a 40% crude yield of Cyclonite was obtained on cooling to 20° C. after dilution. A second crop of material was obtained by chilling the filtrate to 0° C. This was found

chiefly to be methylene-*bis*-benzamide (20 gm. from 33 gm. of hexamine) contaminated with a yellow gum from which it was separated by elution with 2-nitropropane. The purified product melted at 223° to 224° C.

Preparation of Acetamide

A. An 83% yield of acetamide, m.p. 81° to 82° C., could be obtained by stirring 1 equivalent of dry ammonium acetate into 3.5 equivalents of acetic anhydride at 57° C. The temperature of the mixture rose to 71° C. during solution of the salt, and then cooled rapidly. The clear cold solution was evaporated at 25° C. under 760 mm. (atmospheric) to yield pure acetamide.

B. A total of 0.312 mole of ammonium nitrate was heated for 10 hr. with a stirred mixture of 1.7 moles of acetic anhydride and 1.75 moles of acetic acid. This total was added in portions of 0.15 mole at zero time, 0.08 mole after two hours and 0.08 mole after the next hour. The nitrate had all dissolved after four hours. No precipitate appeared after the solution was finally cooled. Distillation at 70° C. under 15 mm. yielded 10 to 15 cc. of yellowish liquid; subsequent distillation at 120° C. yielded 1.35 gm. of acetamide, m.p. 81° to 82° C. (m.m.p.). This yield of 7% may be low because of losses in transfer but could not have exceeded 15%. A small amount of dark brown residue remained in the flask.

When this procedure was varied by concomitant addition of 0.815 mole of 98% nitric acid with the other reagents, no acetamide was obtained; upon cooling, a large part of the ammonium nitrate precipitated. By air evaporation 84.5% was recovered, m.p. 167° to 169° C.

1,5-Diaceto-3,7-endomethylene-1,3,5,7-tetrazacyclooctane, VIII

To 300 gm. (3 moles) of stirred acetic anhydride was added 140 gm. (1 mole) of hexamine. An ice-bath was applied immediately to prevent temperature rise above 56° C. After two hours the reaction mixture had cooled to 25° C. and 100 cc. of ethyl ether was then added. The filtered precipitate, washed with absolute ethanol, weighed 13.7 gm. and melted at 180° C. Crystallization from absolute ethanol gave 9.07 gm. melting at 193.8° to 194° C. The crude yield was 6.5% of theoretical. When addition of hexamine was gradual so that the reaction temperature did not rise above 40° C. the yield was 5.2%. When cooling was not applied and the temperature rose to 95° C., no product at all was obtained. Likewise none of the compound was formed when the gradual addition was carried out while 89 gm. (1 mole) of methylolacetamide was added equivalently (temp. 40° C.).

Repeated purification by solution in chloroform (4 cc. per gm.) and crystallization following addition of 1 volume of ether failed to raise the melting point. After solution in nitromethane (3.5 cc. per gm.) followed by dilution with ether (5.8 cc. per gm.) it melted at 194.0° to 194.2° C. The compound was recovered unchanged after treatment of its chloroform solution with an excess of diazomethane in ether. It was also recovered unchanged by chloroform extraction of its aqueous solution to which one equivalent of alkali had

been added. Calc. for $C_9H_{18}N_4O_2$: C, 50.9; H, 7.60; N, 26.4%. Found: C, 51.1; H, 7.50; N, 25.4%.

A large number of attempts to prepare VIII by interaction of 5 moles of formaldehyde (as paraform, trioxane, or the monomeric gas) with 2 moles of ammonium acetate and 2 moles of acetamide in acetic acid and/or 5 moles of acetic anhydride at temperatures from 25° C. to 70° C. failed to give a trace of the desired product. The result was the same when acetic acid was omitted and also when methylolacetamide was used instead of acetamide.

1,9-Diacetoxy-2,6-diaceto-4,8-dinitro-2,4,6,8-tetrazanonane

To a suspension of 2 gm. (0.0094 mole) of 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane in 10 cc. (0.1 mole) of acetic anhydride at 25° C. was added 1.0 cc. (0.024 mole) of 98% nitric acid. After 10 min. at room temperature, the reaction mixture was warmed five minutes on the steam bath and then drowned in 100 cc. of ice and water. It was then neutralized to pH 4 with ammonia. The precipitated oil was converted to a gummy solid which was dissolved in acetone. Dilution with petroleum ether precipitated 1.83 gm., melting 121.5° to 123° C., or 46% of theoretical on the 1 : 1 mole basis. The material melted at 124° to 124.5° C. after three crystallizations from acetone-methanol (55° to 20° C.). Calc. for $C_{13}H_{22}N_6O_{10}$: C, 37.0; H, 5.27; N, 19.9%. Found: C, 37.0; H, 5.42; N, 19.9%. When only half as much nitric acid was used in this preparation there was no water insoluble product. Dilution of the reaction mixture into ether gave an unstable precipitate which dissolved in boiling methanol. After two minutes, this solution also gave no water-insoluble material.

When diacetoxydiacetodinitrotetrazanonane was dissolved at 0° C. in 30 equivalents of 98% nitric acid and the solution (finally at 10° C.) was drowned in water, no insoluble precipitate appeared.

1,5-Diaceto-3-nitroso-7-nitro-1,3,5,7-tetrazacyclooctane, XI

A solution of 11.5 ml. (0.184 mole) of nitrogen tetroxide in 15.5 ml. (0.373 mole) of 98% nitric acid was maintained at 0° C. while 2.41 gm. (0.012 mole) of 1,5-diaceto-3,7-*endomethylene*-1,3,5,7-tetrazacyclooctane, VIII, was added over seven minutes. There was no appreciable heat evolution. After five minutes more at 0° C. the whole was poured into 400 gm. of ice. No precipitate appeared at once in the clear blue aqueous solution, but after 12 hours 2.46 gm. of product was filtered off. This 75% yield of XI melted at 225.2° to 227.2° C. The compound was photosensitive and turned blue on exposure to diffuse light.

1,5-Diaceto-3,7-dinitro-1,3,5,7-tetrazacyclooctane, IX

A solution of 1.0 gm. (0.0037 mole) of the nitroso compound XI in 7.2 ml. (0.16 mole) of 98% nitric acid was prepared cautiously at 2° to 3° C. It was stirred at this temperature while 2.63 gm. (0.012 mole) of ammonium persulphate was added over five minutes. After 15 min. more at this temperature, it was warmed to 20° C., allowed to stand one hour, and then

poured into ice. After 30 min., a precipitate began to appear; this was filtered off after 75 min. It weighed 0.89 gm. or 83% of the theoretical yield. It melted at 262° to 263° C. and was crystallized three times from boiling nitromethane (60 cc. per gm.) to melt at 265.5° to 266° C. This melting point at 2° per minute temperature rise could be raised or lowered by change in rate. Calc. for $C_8H_{14}N_6O_6$: C, 33.1; H, 4.86; N, 28.9%. Found: C, 33.2; H, 4.92; N, 28.7%.

The procedure of Carmack and coworkers (4) was repeated and the product crystallized repeatedly from boiling acetone, m.p. 261° C. A mixed melting point with IX was not lowered.

This compound was converted in 25% yield to 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) by overnight treatment of 0.26 gm. with 4 cc. of 99% nitric acid. The solution was warmed to 70° C. for five minutes and then poured into ice. The crude product (m.p. 258° C.) was purified by crystallization from 70% nitric acid to melt at 275° to 276° C. A mixed melting point with an authentic sample was not lowered.

When this procedure was varied by use of 95% nitric acid and a final warming to 70° C. with immediate dilution into ice, the product melted at 214° C. and weighed 0.06 gm. This was proved to be a 23% yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane by mixed melting point determination.

Bachmann Nitrolysis of Diacetoendomethylenetetrazacyclooctane, VIII

To a stirred suspension of 1.76 gm. (0.022 mole) of ammonium nitrate in 5.67 cc. (0.06 mole) of acetic anhydride at 65° to 70° C. were added equivalently 1.25 ml. (0.03 mole) of 98% nitric acid and a solution of 2.12 gm. (0.01 mole) of VIII in 5 cc. of acetic acid over 50 min. After a subsequent 10 min. period 0.54 cc. (0.03 mole) of water was added.

After three hours, the suspension was diluted with 15 cc. water and filtered to remove 0.63 gm. melting at 175° to 190° C., density greater than 1.71. This was crystallized from nitromethane to yield 0.35 gm. of Cyclonite, m.p. 195° to 196° C., mixed melting point not lowered.

The aqueous filtrate was neutralized with 50% aqueous potassium hydroxide to pH 9. Filtration yielded 0.44 gm., m.p. 155° to 210° C. Centrifugation showed that its density was less than 1.71. This was dissolved in 20 to 25 cc. hot nitromethane. On cooling, 0.12 gm. of material, m.p. 261° to 262° C. (soft 253° C.), crystallized out. An additional 0.03 gm. was obtained by concentration of the mother liquors to 2 cc. The total yield was crystallized from hot nitromethane and then from acetic acid (140 cc. per gm.) to melt at 263° to 264° C. A mixed melting point with the compound prepared from XI was not lowered.

The remaining 2 cc. of nitromethane solution, from which was isolated the compound described above, was evaporated in vacuum to dryness. The residue weighed 0.11 gm. and melted at 139° to 149° C. Half of this was heated with 0.5 cc. of 70% nitric acid to yield 18 mgm. of impure Cyclonite,

m.p. 185° to 194° C. The other half was suspended in petroleum ether, (b.p. 90° to 100° C.) – ethylene dibromide mixture and centrifuged to give a top layer (0.05 gm.) melting at 141° to 144° C. This was repeatedly crystallized wastefully from nitromethane–ether to give 0.01 gm. melting at 154° C. A mixed melting point with 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane, X, was not lowered. Yield on the basis of the nitric acid decomposition was estimated as 3% of theoretical. The heavier part of the centrifugate proved by mixed melting point to be Cyclonite.

The ratio of reagents was varied in two additional experiments. The results of all three are recorded in Table III, where all percentage yields are on the 1 : 1 molar basis.

TABLE III
YIELD FROM BACHMANN NITROLYSIS OF 1 MOLE OF VIII

Moles HNO ₃	Moles NH ₄ NO ₃	Moles Ac ₂ O	% RDX	% X	% IX
3	2.2	6	17	3	5.2
3.5	2.2	5.3	14	0.8	14
4	2.2	6	25	5	7

Bachmann Nitrolysis of 1-Acetamidomethylhexamine-1 nitrate, IV

A. With Acetic Anhydride

To a stirred solution of 56.6 cc. (0.6 mole) of acetic anhydride and 50 cc. of acetic acid was added over 45 min. 27.4 gm. (0.1 mole) of IV, while a solution of 17.6 gm. (0.22 mole) of ammonium nitrate in 13.25 cc. (0.32 mole) of 99% nitric acid was added proportionately with respect to the solid. The liquid feed was, however, started ahead of the solid feed so that a 2% lead of the former was maintained over the latter.

The solid dissolved in the reaction mixture until addition was about half complete. After that it only partially dissolved; much foaming accompanied the addition of the last third of the solid. After 15 min. subsequent stirring at the reaction temperature (65° to 68° C.) the mixture was cooled, treated with 40 cc. of water, and then evaporated to dryness under 12 mm. pressure. The residue was covered with 40 cc. of water and neutralized to pH 6.4 with 28% aqueous ammonia. The gummy precipitate solidified completely after 12 hr. stirring, during which colorless gas was evolved. The filtered precipitate was ground, dried, and centrifuged in a medium of density 1.70 (ethylene dibromide – petroleum ether) to yield 9 gm. of impure Cyclonite–tetranitrotetrazacyclooctane (HMX) mixture (m.p. 169° C.) which was heavier than the medium. When an aliquot of this was heated with 70% nitric acid, cooled, and diluted, it yielded the equivalent of 8.6 gm. of uncontaminated RDX–HMX, m.p. 193° C. The centrifugate also contained a layer which was lighter than the medium. It weighed 8.75 gm. (m.p. ca. 110° C.). Both crops were fractionally crystallized from acetic acid, from

nitromethane-acetone and from acetone-ether to yield (in addition to the Cyclonite-HMX) 5.5 gm. of impure 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, VI, m.p. 210° to 211° C. This was 90% pure (according to the destruction of VI in hot 70% nitric acid) if it contained only Cyclonite and HMX as impurities. This impure material was recentrifuged in the suspension medium of density 1.70 and then was recrystallized from hot nitromethane-acetone (32 cc. and 20 cc. per gm.) to weigh 4.3 gm. and melt at 225.2° C. A mixed melting point with pure VI was not lowered. The yields based on nitric acid fume-off are therefore about 40% of the theoretical (1 : 1 molar basis) as Cyclonite-HMX and 17% as acetotrinitrotetrazacyclooctane, VI.

The evaporated mother liquors from which these substances were isolated were carefully examined by repeated fractional crystallization from ethanol and nitromethane-ether. While there were undoubtedly low-melting compounds present, our experience with the crystallization of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane persuades us that it was not present.

B. With Propionic Anhydride

When the foregoing procedure was repeated, using propionic rather than acetic anhydride, a fraction melting at 211° to 215° C. was obtained which would represent 5% of the theoretical yield of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane if it had been pure. According to its decomposition in hot 70% nitric acid it contained about 30% of an RDX-HMX component, m.p. 211° to 218° C. A mixed melting point of the 5% yield with authentic acetotrinitrotetrazacyclooctane was not lowered, whereas a comparable melting point with the propionyl analogue was lowered 15° C. A thorough search of all fractions of the product failed to reveal the presence of 1-aceto-3,5-dinitro-1,3,5-triazacyclohexane.

Nitrolysis of 1-Acetamidomethylhexamine-1 nitrate with Nitric Acid and Acetic Anhydride

To a cold solution of 39.3 cc. (0.39 mole) of acetic anhydride in 20 cc. of glacial acetic acid was added with stirring 13.6 cc. (0.314 mole) of 97% nitric acid. This solution was maintained with stirring at 25° ± 4° C. with a cold water bath while 21.5 gm. (0.0786 mole) of IV, m.p. 174° to 175.5° C. was added over 10 min. The whole was stirred an additional two hours at room temperature and then diluted with 75 cc. of water. This solution was neutralized with 12 gm. (0.3 mole) of sodium hydroxide. The aqueous phase was decanted from the gum which thus was precipitated. The gum was digested a few minutes at 40° C. with 75 cc. ethanol, cooled to 15° C., and the solid filtered and dried. It weighed 23 gm., m.p. 113° to 120° C. (decomp.). Yield as this crude VII is 69% of theoretical (1 : 1 basis). The ethanolic filtrate was combined with the aqueous mother liquor.

The crude VII was dissolved in 125 cc. of warm acetone and precipitated with 125 cc. of warm ethanol to give 17 gm. (51% yield), m.p. 144° to 146° C.

(decomp.). Further crystallizations from acetone raised the melting point to 152–153° C. (decomp.). It was identified by mixed melting point (9).

The combined aqueous ethanol liquors were diluted to 600 cc. with water, and extracted with 175 cc. of ether and then with 300 cc. of petroleum ether (b.p. 60° to 90° C.) benzene (1 : 1). The extracts were combined, washed with two 150 cc. portions of water and then with aqueous sodium carbonate and finally dried over anhydrous sodium sulphate. Distillation of the dried extract at 4.5 mm. gave 5.8 gm. of liquid, b.p. 129° to 136° C. (chiefly at 134° C.). The yield calculated as crude diacetoxydimethylnitramine, VII-a (b.p. 152° C. (10 mm.) when pure) is 36% of theoretical on the 1 : 1 molar basis. This material was identified by conversion (6) to dinitroxydimethylnitramine, m.p. 46° to 49° C., in 35% yield.

Reactions Relating to Structure of 1-Acetamidomethylhexamine-1 nitrate, IV.

The salt, IV, was prepared by adding a solution of 140 gm. (1 mole) of hexamine in 200 cc. of acetic acid over 30 min. to a stirred solution of 98 cc. (1 mole) of acetic anhydride and 63 gm. (1 mole) of 97% nitric acid, previously prepared at 0° to 10° C. and maintained below 35° C. After five hours at 25° C., 100 cc. of ethyl ether was added. The gummy precipitate which formed over 12 hr. was dissolved in 270 cc. of water, and 900 cc. of 95% ethanol was added. Filtration at 10° C. after three hours yielded 86 gm. melting at 172.3° to 172.8° C. or 31% of the theoretical.

When 0.27 gm. (0.001 mole) of this compound was dissolved in 36 cc. (0.001 mole) of saturated aqueous styphnic acid solution an immediate precipitate amounting to 0.32 gm. of hexamine styphnate appeared. This 83% yield melted at 194° C. and was identified by mixed melting point.

When 0.05 mole of the salt IV was dissolved in 30 cc. of water at 0° C. it required only 0.0375 mole of alkali before a pH of 10.5 was reached. The odor of formaldehyde was apparent. The solution was evaporated to dryness under 12 mm. pressure and the residue eluted with 50 cc. of hot chloroform. Evaporation of this solvent yielded 6.38 gm. of impure hexamine. The basicity of the amine could therefore not be determined, since it was not stable, but a *M*/10 aqueous solution free from carbon dioxide, was tested against a glass electrode to show a pH of 6.99.

When a solution of 0.004 mole of IV in 9 cc. water and 10 cc. of ethanol at 0° C. was treated with 0.0045 mole of diazomethane in ether, the solution became colorless in 90 sec. but 75% of pure IV could be recovered from the gummy product. None could be recovered from the colorless solution after 0.02 mole of diazomethane was added to a similar water-ethanol solution of IV over 22 min.

By contrast a solution of 0.004 mole of hexamine mononitrate in 9 cc. water and 10 cc. of ethanol reacted instantly with 0.0045 mole of ethereal diazomethane. When the solution medium was altered to 3 cc. water and 13 cc. of ethanol, evaporation of the solution after diazomethane treatment left a

residue from which 36% of the theoretical yield of hexamine methonitrate could be obtained by crystallization from ethanol.

Bachmann Nitrolysis of 1-Propionamidomethylhexamine-1 nitrate

The Bachmann nitrolysis was effected with 0.44 mole acetic anhydride in 34 cc. acetic acid, 0.15 mole ammonium nitrate in 0.22 mole 99% nitric acid and 0.068 mole of 1-propionamidomethyl-hexamine-1-nitrate (1), m.p. 177° to 178° C. The crude product (14.4 gm., m.p. 162° to 172° C.) was found to contain 60% of the theoretical yield of RDX-HMX when an aliquot was boiled with 70% nitric acid. The main bulk was centrifuged in aqueous zinc chloride (d. 1.70) and the light fraction crystallized from acetone-ethanol and from nitromethane to yield 1.44 gm. of 1-propanoyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, m.p. 198.5° to 199.5° C. (7% of theory, 1 : 1 mole basis), identified by mixed melting point. The low yield is caused by wasteful crystallization which did, however, establish the absence of 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane among the reaction products.

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THE HALF LIFE OF C^{14}

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Abstract

Compensated gas counters of known efficiency, filled with carbon disulphide and carbon dioxide containing a mass-spectrometrically determined proportion of $C^{14}O_2$, have been used to determine the half life of C^{14} . The half life has been found to be 6360 ± 200 years.

Introduction

Within the last two years experiments to determine the half-life of C^{14} have been reported by Reid, Dunning, Weinhouse, and Grosse (10) and by Norris and Inghram (7, 8). The former authors obtained a value of 4700 years, and the latter, values of 6100, 5300, and 5100 years. The value of 5100 years obtained by Norris and Inghram (8) supersedes those previously obtained by the same authors (7).

To determine the half life of a long-lived radioactive isotope of an element such as C^{14} , the values of dN/dt and N in the relation $dN/dt = -\lambda N$ must be measured. In the experiments referred to above, the disintegration rate, dN/dt , was measured using an end-window type of Geiger-Müller counter and the number of C^{14} atoms, N , present at time t , was determined by means of a mass spectrometer.

The use of an end-window type of Geiger-Müller counter with an external source for the absolute measurement of radioactive disintegration rates is always open to some doubt, even with sources emitting energetic beta particles, owing to the corrections that have to be made for absorption, including self-absorption, and back-scattering. In the case of a low energy beta particle emitter, such as C^{14} , these corrections become more important and the value obtained for the disintegration rate becomes more uncertain.

The uncertainties due to absorption and back-scattering are eliminated by the use of a gas counter of the type described by Miller (1, 6). To provide C^{14} standards for this project, use was made of such gas counters to determine the absolute disintegration rate. Absolute measurements of the disintegration rate of C^{14} , in the form of carbon dioxide, can be made provided the internal efficiencies of these counters are known. Extensive experiments have been carried out to determine the internal efficiency of a Miller type gas counter.* From the results of these experiments, together with a mass spectrometric determination of N , a new value for the half life of C^{14} has been obtained.

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* See succeeding paper.

Production of C^{14}

To produce significant quantities of high specific activity C^{14} , a rather large amount of a suitable nitrogen-containing compound must be irradiated in a high thermal neutron flux for a considerable time. The C^{14} which is formed from the nuclear transformation $N^{14}(n, p)C^{14}$ must then be extracted. Methods for production of C^{14} from neutron irradiated ammonium nitrate solution and beryllium nitride have been reported in the literature (9, 12). From considerations of stability, undesirable nuclear reactions on irradiation, purity, and ease of extraction, solid potassium nitrate has been selected as the most suitable compound for irradiation in the Chalk River pile for the production of C^{14} .

Reagent grade potassium nitrate was melted in a stainless steel pot and cast into rods 6 in. long and 1.25 in. in diameter, using a stainless steel mold. These rods were slid into a long aluminum cylinder, which was sealed and which then served as the irradiation container. This material was then exposed to a total thermal neutron irradiation of approximately 2×10^{19} neutrons per sq. cm.

The C^{14} produced in the potassium nitrate under these conditions appears to be present entirely as carbonate ion or as carbon dioxide trapped in the crystal structure, since carbon dioxide is the only active carbon compound it has been possible to obtain from the irradiated potassium nitrate. This could be expected from theoretical considerations such as those discussed by Libby (3). During irradiation the potassium nitrate also decomposed into nitrite and oxygen to a slight extent. To extract the C^{14} , the irradiated potassium nitrate rods were dissolved in 1 *N* nitric acid containing 5% by weight of hydrogen peroxide. This solution oxidizes the small amount of nitrite ion and almost completely prevents the formation of nitrogen dioxide. The oxygen and carbon dioxide were swept into carbonate-free sodium hydroxide solution (2) with carbon-dioxide-free air. Barium carbonate was then precipitated by the addition of barium chloride solution and the solid barium carbonate washed with boiled distilled water. To obtain a purer, more uniform source of C^{14} , carbon dioxide was regenerated from the barium carbonate with boiled dilute nitric acid and reabsorbed in 0.5 *N* carbonate-free sodium hydroxide. Precautions were taken at all times to prevent contamination with inactive carbonate and included carrying out extraction operations in carbon-dioxide-free air or in nitrogen. The 0.5 *N* sodium hydroxide solution was used as the source of C^{14} .

Preparation of Carbon Dioxide Sample

In view of the different amounts of C^{14} required for the mass-spectrometric and counting experiments the carbon dioxide samples for each had to be prepared separately, the C^{14} content for the latter experiments having to be accurately diluted by a factor of the order of 10^4 .

Samples of carbon dioxide for the determination of the absolute disintegration rate were prepared in the following manner. An aliquot of the 0.5 N sodium hydroxide solution of C^{14} was diluted to a known volume with a solution of sodium carbonate carrier of known strength. An aliquot of this diluted solution was transferred to a long narrow Pyrex test tube containing a weighed amount of anhydrous sodium carbonate (0.5 gm.) and the tube shaken until the carbonate dissolved. By this method of dilution isotopic homogeneity is assured. A small quantity of carbonate-free sodium hydroxide solution was added to maintain a pH greater than 10. The solution was then evaporated and dried at 140° C. Carbon dioxide was generated from the residue by ignition with excess lead chloride and the resulting carbon dioxide collected in a sample tube by freezing with liquid nitrogen. Three such samples were prepared.

The carbon dioxide for the mass-spectrometric determination of the abundance of C^{14} was prepared as follows. Two aliquots of the 0.5 N sodium hydroxide solution containing C^{14} as sodium carbonate were taken. The C^{14} in each was precipitated as barium carbonate by the addition of barium chloride. The barium carbonate was separated by centrifuging, carefully washed with water and ethyl alcohol,* and dried at 140° C. After weighing, the precipitate was again dried at 240° C. and reweighed. Any C^{14} remaining in the combined supernatant liquid and wash solutions for each aliquot was recovered by addition of carbonate carrier as sodium carbonate followed by washing, drying, and weighing as before. The samples were then transferred to a vacuum system for conversion to carbon dioxide. The two precipitates from the original solutions were outgassed at 200° C. and converted to carbon dioxide (samples 4a and 5a, Table III) by ignition in a quartz tube at 1000° to 1200° C. Ignition was continued until no further carbon dioxide was evolved. All the carbon dioxide was collected by freezing with liquid nitrogen. The precipitates from the combined supernatant and wash solutions were separately converted to carbon dioxide (samples 4b and 5b, Table III) by ignition in a Pyrex tube with approximately five molecular proportions of carbonate-free lead chloride.† Such a mixture forms a liquid melt that rapidly evolves carbon dioxide at about 350° C.

The Counting Equipment

The gas counters used were of the compensated type that have already been described (5). These counters were designed to eliminate end errors due to field distortion and to beta particles entering the counting volume from the space outside the cathode. The units used were of extremely simple design, being assembled from copper tubing and glass spacers in the manner indicated in Fig. 1. Two sets of such counters were used, one set consisting

* It should be noted that the molecular structure of ethyl alcohol is such as to preclude the exchange of carbon atoms with the barium carbonate.

† The use of lead chloride for the conversion of barium carbonate to carbon dioxide was suggested in a private communication from F. T. Bonner and S. O. Thompson, Brookhaven National Laboratory, through L. Yaffe, National Research Council, Chalk River, Ontario.

of a long and a short cathode of 1.167 cm. diameter and the second set having cathodes of 1.384 cm. diameter. In each compensated unit of two counters the long cathode was 6 in. long and the short cathode was 2 in. long. The geometries of the ends of the long and short counters of each unit should, in order to eliminate end effects, be constructed similarly and this, with the design illustrated in Fig. 1, is readily accomplished.*

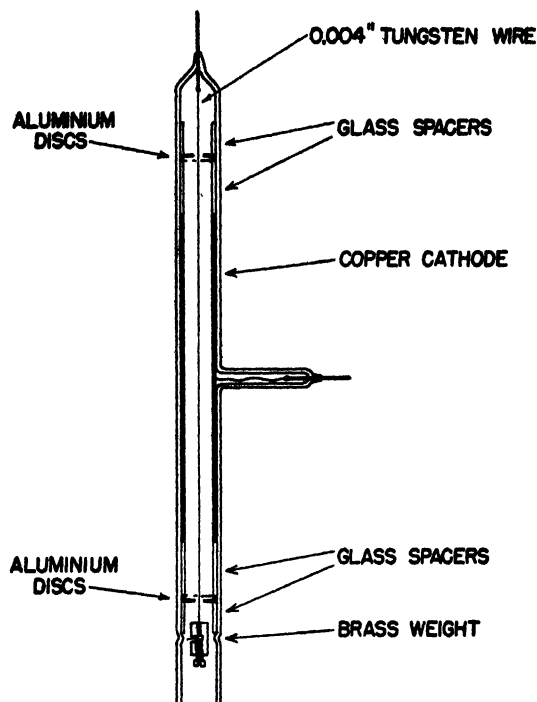


FIG. 1. Section through gas counter tube.

Measurements were carried out with these counters using filling mixtures of about 20 cm. of mercury pressure of carbon dioxide and a little under 1 cm. of mercury pressure of carbon disulphide. Such mixtures are nonselfquenching so that it was necessary to use external quenching, provided in the form of a Parkinson multivibrator quenching unit (5). The high voltage for these counters was provided by a stabilized 4000 v. power unit, type 200†, and the number of counts was registered by means of a Dynatron scale-of-a-hundred

* Instead of using separate long and short units a more convenient form of such a counter could be constructed in the manner indicated in Fig. 1 but with the two cathodes in the same glass tube. Such a counter would be assembled as follows (proceeding from the top down): glass tube; two aluminum disks as in Fig. 1; 1-in. long glass spacer; long (6 in.) cathode; 1-in. long glass spacer; thin aluminum disk, with 1/64 in. hole, to center the wire and to separate counter volumes; 1-in. long glass spacer; short (2 in.) cathode; 1-in. long glass spacer; two aluminum disks as at bottom of Fig. 1. The same 0.004 in. tungsten wire would then be stretched through both counters.

† These are T.R.E. designed instruments assigned these type numbers by the U.K. Ministry of Supply. The model used was manufactured by Dynatron Radio Ltd., of Maidenhead, England. The units are voltage stabilized to $\pm 2\%$ of maximum voltage on any range and input regulation such that $\pm 10\%$ variation in line voltage produces variation in output voltage of not more than $\pm 0.56\%$.

scaling unit, type 200. A quench time of about 400 $\mu\text{sec.}$ was found to give satisfactory plateaux.

The filling of the counters was carried out by means of a vacuum system and the counters were isolated from the rest of the system by means of mercury valves. The pressure of gas in the system was measured by means of a mercury U-tube manometer made from glass tubing of 1 cm. bore, the readings of which could be made reproducibly to 0.01 cm. using a cathetometer. The transfer of carbon dioxide or carbon disulphide from one part of the vacuum system to another was accomplished by freezing in liquid nitrogen.

Subsidiary experiments have been carried out using a compensated counting unit having cathodes 18 in. and 14.5 in. long and 3 in. in diameter in order to determine the efficiency of such gas counters. For additional confirmation, readings at different gas pressures were also obtained. The results of these and other experiments, which were extensive in nature and which were designed to check the efficiencies of the counters, will be published separately, but strong evidence has been obtained to prove that these counters do in fact have an efficiency that is not significantly less than 100%.

Disintegration Rates

Measurements were made on three samples of carbon dioxide containing C^{14} . The results obtained with one of these samples (Sample 1) are shown in Fig. 2 in which the plateaux are plotted for each of the four counters.

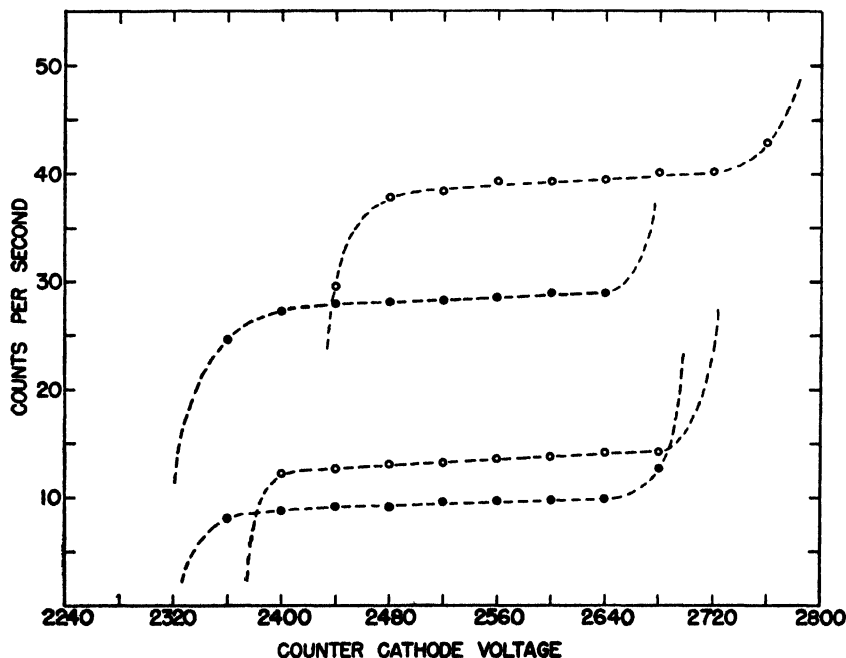


FIG. 2. Plateaux for narrow and wide compensated counting units. Solid circles show results for short and long 1.167 cm. counters; open circles results for short and long 1.384 cm. counters. Pressure of carbon dioxide is 19.36 cm. of mercury at 25° C. and that of carbon disulphide is 0.89 cm. of mercury at 25° C.

It will be observed that none of the plateaux shown in Fig. 2 are completely flat. This appears to be due to the attenuation of the electric field at each end of the counting volume. As the cathode is made more negative so will the electric intensity at the ends of the anode wire be increased, and the effective counting volume be extended to fill a greater proportion of the cathode volume. If the end geometries for both the short and long counters are similar, then the variation of field at the ends of the cathodes with changing cathode voltage will also be similar. The increase in counts due to this effect, with increasing voltage across the counter, should therefore be the same for both the long and short counters of either unit, and the difference in the counting rates of the long and short counters of a unit (taken at the same voltage) should remain constant with increasing voltage in the Geiger region.

In Table I this differential count for different cathode voltages is shown for both the narrow and wide counter units. These results are obtained from

TABLE I

Cathode volts (negative)	Wide counter unit (counts per second)			Narrow counter unit (counts per second)		
	Long counter	Short counter	Differential count	Long counter	Short counter	Differential count
2400		12 20		27 30 \pm 0 19	8 75 \pm 0 09	18 55 \pm 0 21
2440	29 62	12 66		28 00	9 22	18 78
2480	37 88 \pm 0 25	13 02 \pm 0 08	24 86 \pm 0 26	28 10	9 08	18 02
2520	38 48	13 24	25 24	28 42	9 61	18 81
2560	39 28	13 54	25 74	28 61	9 74	18 87
2600	39 29	13 84	25 45	29 01	9 84	19 17
2640	39 48	14 16	25 32	29 02	9 91	19 11
2680	40 11	14 28	25 83		12 77	
2720	40 24	14 84	25 40			
2760	42 95	—				
2790	—					

the same data as were used to plot the plateaux of Fig. 2. It will be seen that within the limits of experimental error the differential count is constant with increasing counter voltage. The differential volume, i.e., the difference in volume between the long and short cathode volumes, is equal to 15.09 cm.³ for the wide counters and 10.79 cm.³ for the narrow counter unit. The differential volume of 15.09 cm.³ is thus seen, from Table I, to give rise to 25.41 \pm 0.10 counts per second while the differential volume of 10.79 cm.³ corresponds to 18.76 \pm 0.08 counts per second. Errors shown are probable errors based on the total number of counts taken. The counts per second per unit volume of Sample 1 at the pressure of the experiment are therefore 1.68 \pm 0.01 and 1.74 \pm 0.01, respectively, for the wide and narrow counting units. The agreement between these results for counters of different radii shows that errors arising from the loss of counts at the cathode walls are either small or completely absent.

Similar measurements were carried out on Samples 2 and 3, with the results shown in Table II. The dead time of the quenching circuit was increased to 4.2 milliseconds for the measurements on Sample 3. The errors shown in Table II are also probable errors.

TABLE II

Sample	Gas pressure* in counter (cm. Hg at 25° C.)		Differential counts per sec. per cm. ³		Average counts per sec. $\times 10^{-6}$ per ml. of 0.5 N NaOH solution of $Na_2C^{14}O_3$
	CO ₂	CS ₂	1.167 cm. diam. counters	1.384 cm. diam. counters	
1	19.36	0.89	1.738 ± 0.009	1.684 ± 0.011	1.62 ± 0.03
2	20.04	0.52	0.868 ± 0.015	0.860 ± 0.014	1.57 ± 0.03
3	14.53	1.03	1.298 ± 0.007	1.257 ± 0.007	1.61 ± 0.03

* Pressures corrected from temperature inside lead castle to 25° C.

Mass Spectrometric Analysis

The carbon dioxide was analyzed in a 180° Nier type mass spectrometer. The ion beams were scanned by automatic variation of the magnetic field and the intensities corresponding to masses 44, 45, and 46 automatically recorded (4, 11). The intensity of the mass-48 ion beam was not recorded because of uncertainties in the background for this mass. A typical recorder tracing for a normal carbon dioxide sample and for one containing C^{14} in approximately 6.2% abundance are shown in Figs. 3 and 4.

The results of the mass-spectrometric analyses are given in Table III.

TABLE III

ISOTOPIC ABUNDANCE RATIOS AND PERCENTAGES

Sample	Ratio $\frac{\text{Mass 44}}{\text{Mass 46}}$	Ratio $\frac{\text{Mass 44}}{\text{Mass 45}}$	Per cent C^{14***}	Per cent C^{14} corrected
4a (1st precipitation)	14.29 ± 0.02	85.86 ± 0.02	6.08 ± 0.01	6.10
4b (2nd precipitation)	228.2 ± 0.7	85.33 ± 0.04	0.013 ± 0.002	0.01 ₃
5a (1st precipitation)	13.91 ± 0.01	85.91 ± 0.01	6.24 ± 0.01	6.27
5b (2nd precipitation)	213.6 ± 0.2	85.84 ± 0.02	0.043 ± 0.001	0.04 ₃
Normal CO ₂ A*	235.6 ± 0.3	85.67 ± 0.06	—	—
B**	236.2 ± 0.40	85.67 ± 0.03	—	—

* In equilibrium with Lake Ontario water.

** In equilibrium with Ottawa River water.

*** Not corrected for mass-48 contribution.

The method of preparation of the samples was such that the oxygen of mass 18 should be in equilibrium with oxygen from the water of the Ottawa River. The contribution of oxygen 18 to the mass-46 peak would, therefore,

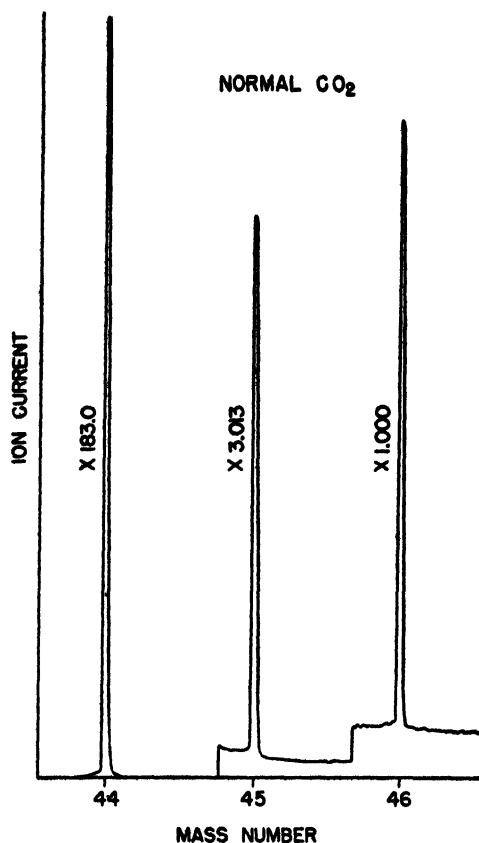


FIG. 3. Mass-spectrometer recorder tracing. Shunt factors are shown alongside each peak.

be the same as for normal carbon dioxide. The contribution of C^{13} to mass 46 is negligible since it depends upon the low abundance of O^{17} . The fact that the ratio of mass 44 to mass 45 (i.e., of C^{12} to C^{13} , neglecting the $C^{12}O^{18}O^{17}$ contribution of 0.08%) remains constant for both the inactive and C^{14} -enriched samples (Table III) means that the C^{12} and C^{13} in the enriched sample arise from carbonate impurity in the reagents used in the production of C^{14} ; no significant amount of C^{13} can have been produced by neutron capture by C^{12} . This is also borne out by the known low neutron capture cross section of C^{12} . This correction has been made with sufficient accuracy by calculation, using the known O^{18} abundance for the normal sample and the approximate percentage of C^{14} . The C^{14} percentages corrected in this manner are given in the last column of Table III.

The values of N , the number of C^{14} atoms per milliliter of original solution, as calculated from the mass-spectrometer data and the weights of the precipitates, are shown in Table IV.

The difference in the per cent C^{14} obtained for the first precipitation on each sample may be due to fractionation of the carbon isotopes during the precipitation as barium carbonate. The possibility that the difference can be due to absorption of atmospheric carbon dioxide by the solution is considered unlikely on the basis of the experimental conditions, the separations having been carried out in an atmosphere of nitrogen. It is even more

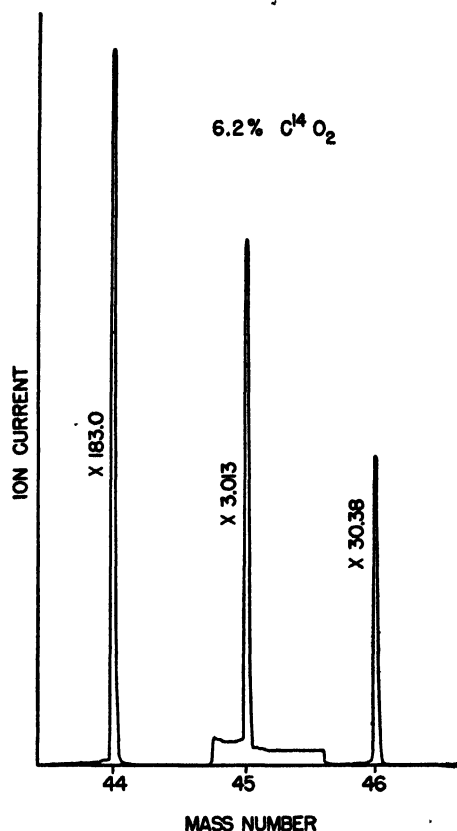


FIG. 4. Mass-spectrometer recorder tracing. Shunt factors are shown alongside each peak. It should be noted that the sensitivity for mass 46 is about one-thirtieth of that for mass 44 in Fig. 3.

TABLE IV

C^{14} ATOMS PER MILLILITER OF ORIGINAL 0.5 N
SODIUM HYDROXIDE SOLUTION OF C^{14}

Sample	N
4a + 4b	$4.76 \pm 0.03 \times 10^{17}$
5a + 5b	$4.77 \pm 0.03 \times 10^{17}$

unlikely that C^{14} could have been lost from either sample. The agreement in the final values obtained for the number of C^{14} atoms per milliliter of original solution supports the possibility of isotopic fractionation.

The Half life of C^{14}

On substituting the mean value of dN/dt equal to 1.60×10^8 disintegrations per second, from Table II, and the mean values of N equal to 4.77×10^{17} atoms of C^{14} , from Table IV, into the relation $dN/dt = \lambda N$, a value for λ of 3.35×10^{-12} sec.⁻¹ is obtained. This corresponds to a half-life of 2.07×10^{11} sec. or 6560 ± 200 years.

The results obtained with the 6.998 cm. diameter counters would, if used to calculate the half life of C^{14} , be in very close agreement with those obtained with the 1.167 cm. diameter counters (see Table II of succeeding paper).

The efficiency of the 1.167 cm. diameter counters has been found to be about 97% (see succeeding paper). This efficiency gives a half life for C^{14} of 6360 ± 200 years.

Acknowledgments

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ON THE EFFICIENCY OF GAS COUNTERS FILLED WITH CARBON DIOXIDE AND CARBON DISULPHIDE¹

R. C. HAWKINGS, R. F. HUNTER, AND W. B. MANN

Abstract

The efficiencies of compensated gas counters filled with carbon dioxide and carbon disulphide have been investigated for the purpose of determining absolute disintegration rates of $C^{14}O_2$ samples. In addition to comparing compensated counting units of different radii, a special counter has been constructed to determine the efficiency at different radii using a collimated beam of electrons from Tl^{204} . The carbon dioxide and carbon disulphide filled counters have been shown to be at least 97% efficient.

Introduction

Measurements that have been made to determine absolute activities of C^{14} in samples of carbon dioxide using gas counters have necessitated a very extensive investigation into the internal efficiencies of such counters.

In using such counters it is necessary to take into consideration two possible sources of error, namely, that due to end effects and that due to the possibility of C^{14} disintegrations near the counter walls giving rise to beta particles that enter the wall without creating enough ion pairs to register a count.

It is the purpose of this paper to give a brief description of the conditions under which such counters can be used to give reliable quantitative measurements.

The Filling Mixtures

The counting equipment is the same as that which has been previously described consisting of a stabilized negative (or positive) 4000 v. H.T. set, Parkinson quencher (4), and scale-of-one-hundred scaler.

To determine the best mixtures of carbon dioxide and carbon disulphide with which to fill the counters preliminary experiments were carried out with a single 0.5 in. diameter platinum tube counter having a 0.004 in. diameter tungsten wire anode. With this counter it was found that plateaux could be obtained with any mixture of the two gases varying from practically 100% carbon dioxide to 100% carbon disulphide. The results that were obtained using these gases undiluted and also a mixture of 50% carbon dioxide and 50% carbon disulphide are shown in Fig. 1.

While the results for carbon dioxide are given as nominally for undiluted gas they were obtained after the counters had been used for a carbon dioxide and carbon disulphide mixture. After pumping out this mixture pure carbon dioxide was admitted but it is felt that a trace of carbon disulphide was probably present since, after further and very extended pumping, plateaux

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could not be obtained with pure carbon dioxide. The different plateaux shown in Fig. 1 for each mixture are for different quench times Q of the quenching equipment.

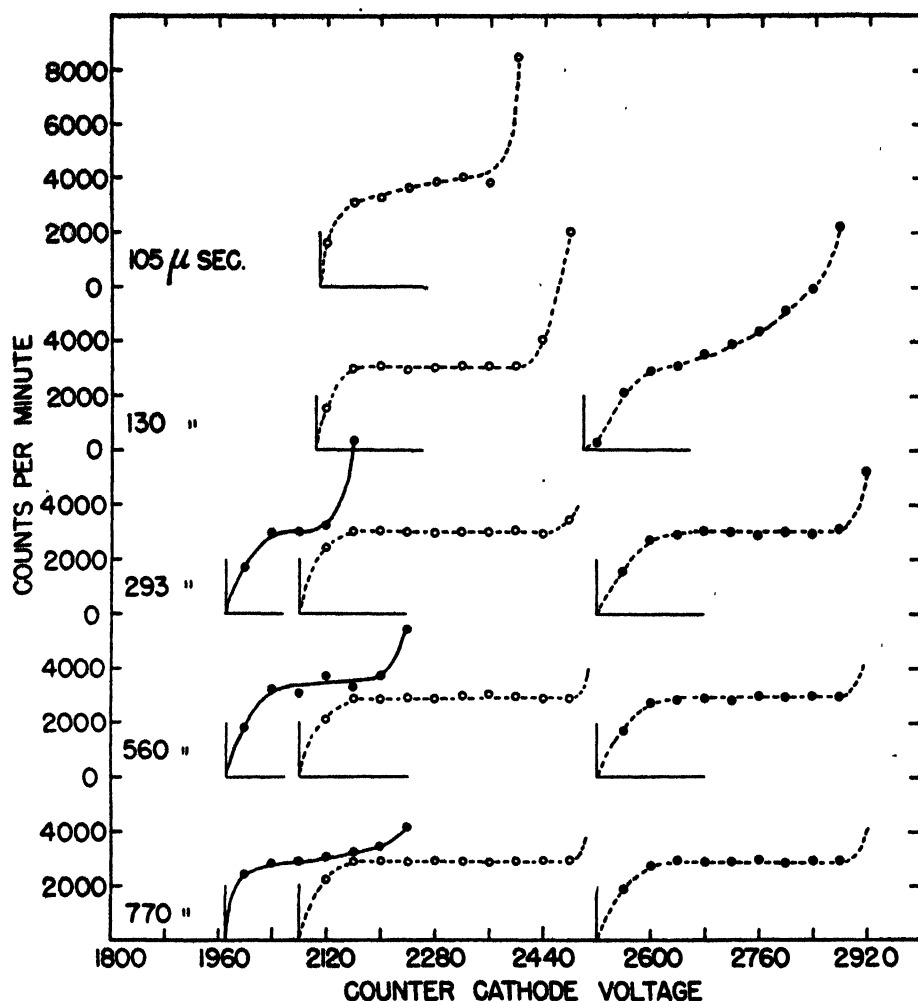


FIG. 1. Effect of varying proportions of carbon dioxide and carbon disulphide. Solid circles represent "pure" carbon dioxide (left) and pure carbon disulphide (right). Open circles represent 50% carbon dioxide mixed with 50% carbon disulphide. The total pressure in every case was about 10 cm. of mercury. The quench period of the external quenching circuit was varied from 105 to 770 μ sec. and that corresponding to each set of curves is shown on the left; all curves on the same horizontal have the same quench period.

For most practical purposes it is necessary to use fillings that shall be predominantly carbon dioxide since the active C^{14} can be more readily converted into carbon dioxide than into carbon disulphide. It is seen from Fig. 1, that "pure" carbon dioxide (with much less than 0.001 cm. of mercury pressure of carbon disulphide) gives plateaux that are a little shorter than is desirable for accurate and reproducible measurements. The addition of approximately only 0.001 cm. of mercury of carbon disulphide serves to give excellent plateaux as shown in Fig. 2. The pressures of carbon dioxide for Curves (a),

(b), (c), and (d) are approximately 5, 10, 15, and 20 cm. of mercury, respectively; thus for most practical purposes the small pressure of carbon disulphide can be neglected. At 20 cm. of mercury pressure instability

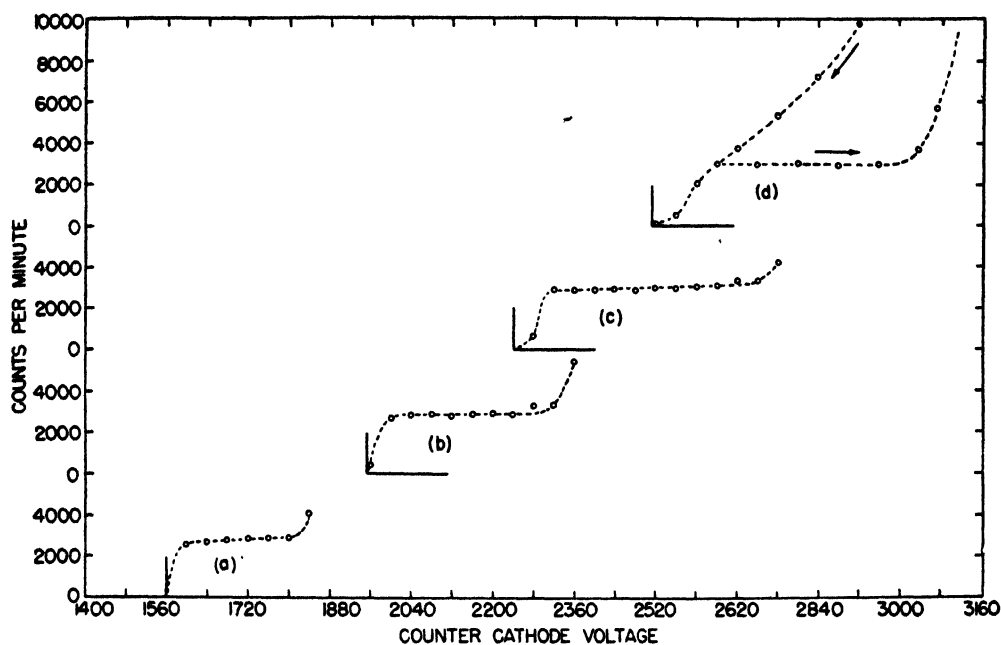


FIG. 2. Plateaux with carbon dioxide fillings mixed with carbon disulphide at 0.001 cm. of mercury pressure. Pressure of carbon disulphide approximately (a) 5, (b) 10, (c) 15, and (d) 20 cm. of mercury. Alternate points on each curve were obtained with increasing and decreasing values of the applied voltage. Curve (d) shows instability in that after exceeding the plateau or increasing voltage the counts do not fall to the plateau again until the voltage is substantially reduced.

became apparent. This was removed, however, by increasing the pressure of carbon disulphide to 0.01 cm. of mercury (Fig. 3).

The effect on threshold voltage obtained by varying the relative proportions of carbon dioxide and carbon disulphide is shown in Fig. 4. The curve for carbon dioxide at 20 cm. of mercury is in agreement with the curve shown by Brown and Miller (1) for carbon dioxide at the same pressure.

The End Correction

Brown and Miller found that, for counters of different length, the counting rate multiplied by V_T/V_C , where V_T was the total counter volume and V_C the cathode volume, was proportional to the number of gram molecules of carbon dioxide, containing a fixed proportion of active carbon dioxide. This would seem to imply that their end correction was small or insignificant.

In the present experiments compensated counter units (4) have been used. If L be the length of the long counter and l that of the short counter comprising the unit, then the difference in counting rates for the long and short counters, when they are filled with the same mixture of active gas, divided by $L - l$

should give the counting rate per unit length for an "ideal" or infinitely long counter.

If this "ideal" counting rate per unit length be multiplied by L , then the difference from the observed count for the long counter will give the end

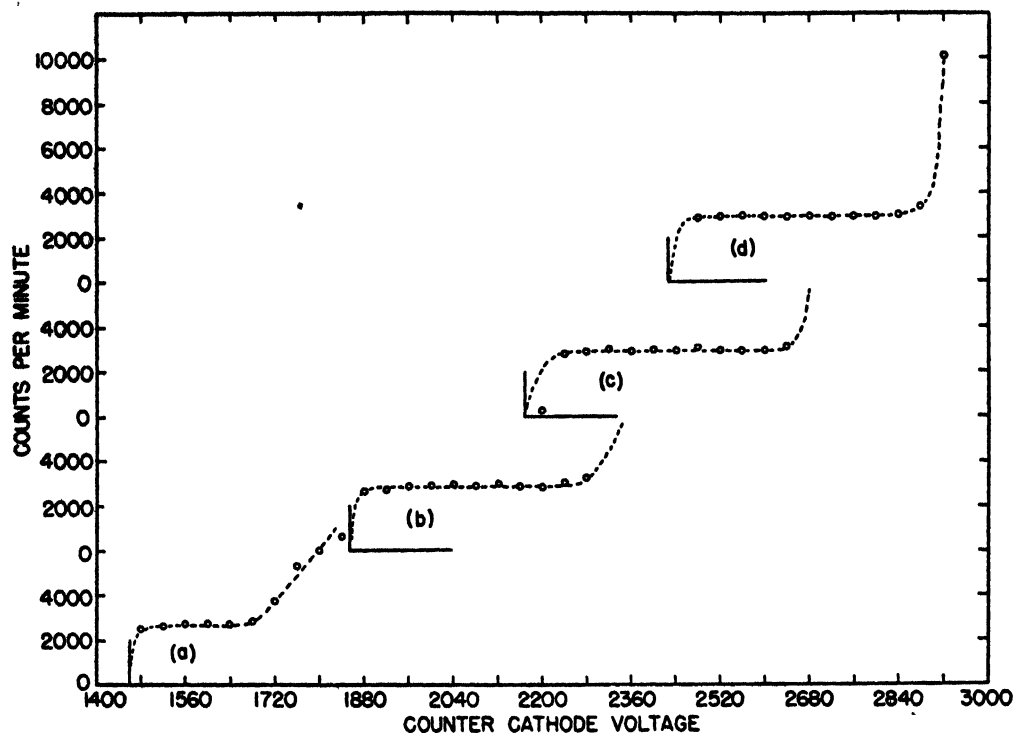


FIG. 3. Plateaux with carbon dioxide fillings mixed with carbon disulphide at 0.01 cm. of mercury pressure. Pressure of carbon dioxide approximately (a) 5, (b) 10, (c) 15, and (d) 20 cm. of mercury. Alternate points on each curve were obtained with increasing and decreasing values of the applied voltage.

correction directly. The same may be done for the short counter and if compensation has been achieved the end effect should be the same in each case. Typical results obtained on doing this for counters of different lengths and radii are shown in Table I. It should be noted that all counters were

TABLE I

Counter radius, cm.	Counter length, cm.	Counts per sec.	"Ideal" counts, N/sec./cm.	Length \times N, counts/sec.	End corrections, counts/sec.
3.499	45.65	53.6	1.313	59.9	6.3
3.499	36.74	41.9		48.2	6.3
0.697	15.22	19.74	1.292	19.70	-0.04
0.697	5.19	6.77		-6.72	-0.05

constructed with a 1 in. glass spacer between the cathode and the aluminum disk which centered the anode wire at each end. In other words the end volumes extend 1 in. beyond the cathode in all counters.

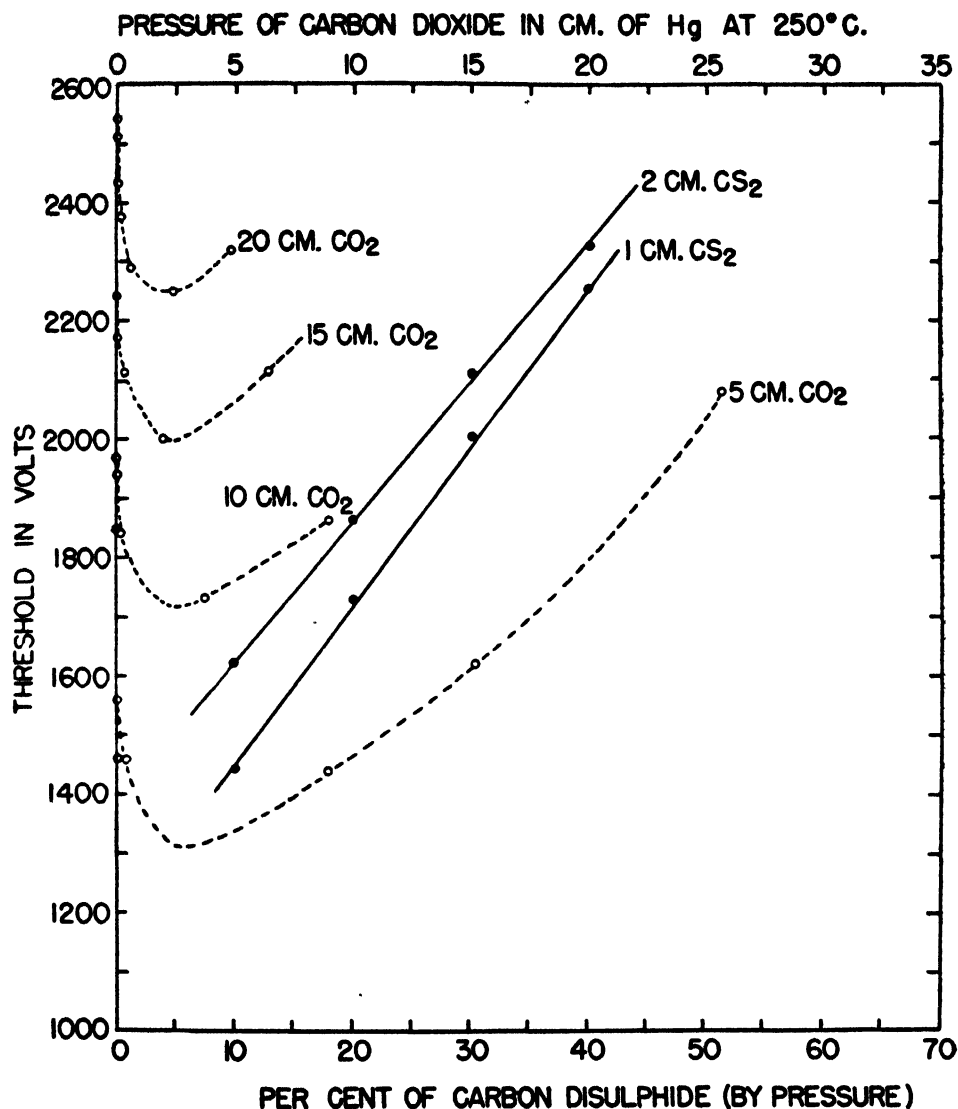


FIG. 4. Threshold voltages for different mixtures of carbon dioxide and carbon disulphide. The lower abscissae refer to the dotted curves for constant pressures of carbon dioxide. The upper abscissae refer to the solid curves for constant pressures of carbon disulphide.

The change in sign of the end correction, shown in Table I, is interesting and indicates that under certain circumstances the end correction for a small diameter counter may be zero.

The end correction will be comprised of two parts, namely, a negative correction for particles entering the active counting volume from the "dead" volume at each end and a positive correction for counts lost by the attenuation of the electric field at each end of the cathode.

With a large diameter counter the positive correction due to field distortion would be expected to be greater than that for particles entering the end. On the other hand, when one increases the applied voltage and moves along the plateau the electric field at the cathode ends increases and the active volume increases. The counting rate will increase and the positive correction that has to be made because of losses inside the cathode volume at each end decreases. At some point the positive and negative corrections may be equal; such a condition seems to have been attained with the compensated counting unit of small diameter in Table I. It would also seem that Brown and Miller have used a point on their plateau that appears to have effected such a compromise. In general, however, it is probably more definite to eliminate the end correction entirely by using compensated counters.

The Radius Correction

It is possible that a C^{14} nucleus disintegrating near the cathode may project a beta particle towards the cathode wall and that it may enter the cathode without initiating an electron avalanche. Assuming a pressure of carbon dioxide of about 20 cm. of mercury it is possible to calculate the probable order of magnitude of this effect.

The average energy of the C^{14} beta particles is about 50,000 v., i.e., about one-third the maximum energy. This energy corresponds approximately to an ion-pair formation of 200 per cm. path in air at N.T.P. (5). A number of authors (2, 3, 6)* have shown that the ionization produced in carbon dioxide by alpha particles is not very different from that produced in air. It has been assumed therefore that the same will also be true for beta particles, at least to the degree of accuracy required in this approximate calculation.

The equivalent ion-pair formation in carbon dioxide by a C^{14} beta particle at 20 cm. of mercury pressure will, therefore, be of the order of 50 per cm. or one ion pair per 0.2 mm. of path. Thus less than half of the C^{14} nuclei disintegrating within approximately 0.2 mm. of the cathode will not give rise to counts. In a counter with a 0.5 in. diameter this gives a count that is too low by not more than 6.5% while the corresponding error for a 3 in. diameter cathode is only 1%.

To demonstrate that the inefficiency of the counters due to this radius effect was not greater than the calculated value the large diameter compensated counting unit already referred to in Table I was assembled. A photograph of two such counters is shown in Fig. 5. The dimensions of the counters used are given in Table I.†

* We are indebted to Mr. J. Dainty for drawing our attention to the work of these authors.

† To obtain satisfactory plateaux with these counters it was necessary to increase the quench period Q of the Parkinson quencher to 4 or 5 milliseconds. This was achieved by increasing C_1 to 0.003 and C_2 to 0.01 μ f. (4).

For lower quench periods the 6.998 cm. diameter counters gave a very high count for an applied voltage only a little above the threshold. This then dropped to a normal counting rate and gave a normal plateau on increasing the voltage. This peak at the low voltage end of the plateau is probably due to the fact that the positive ion sheath does not quite reach the cathode before the voltage is applied again after the quench period. This peak disappeared on increasing the quench period to about 4.2 milliseconds.

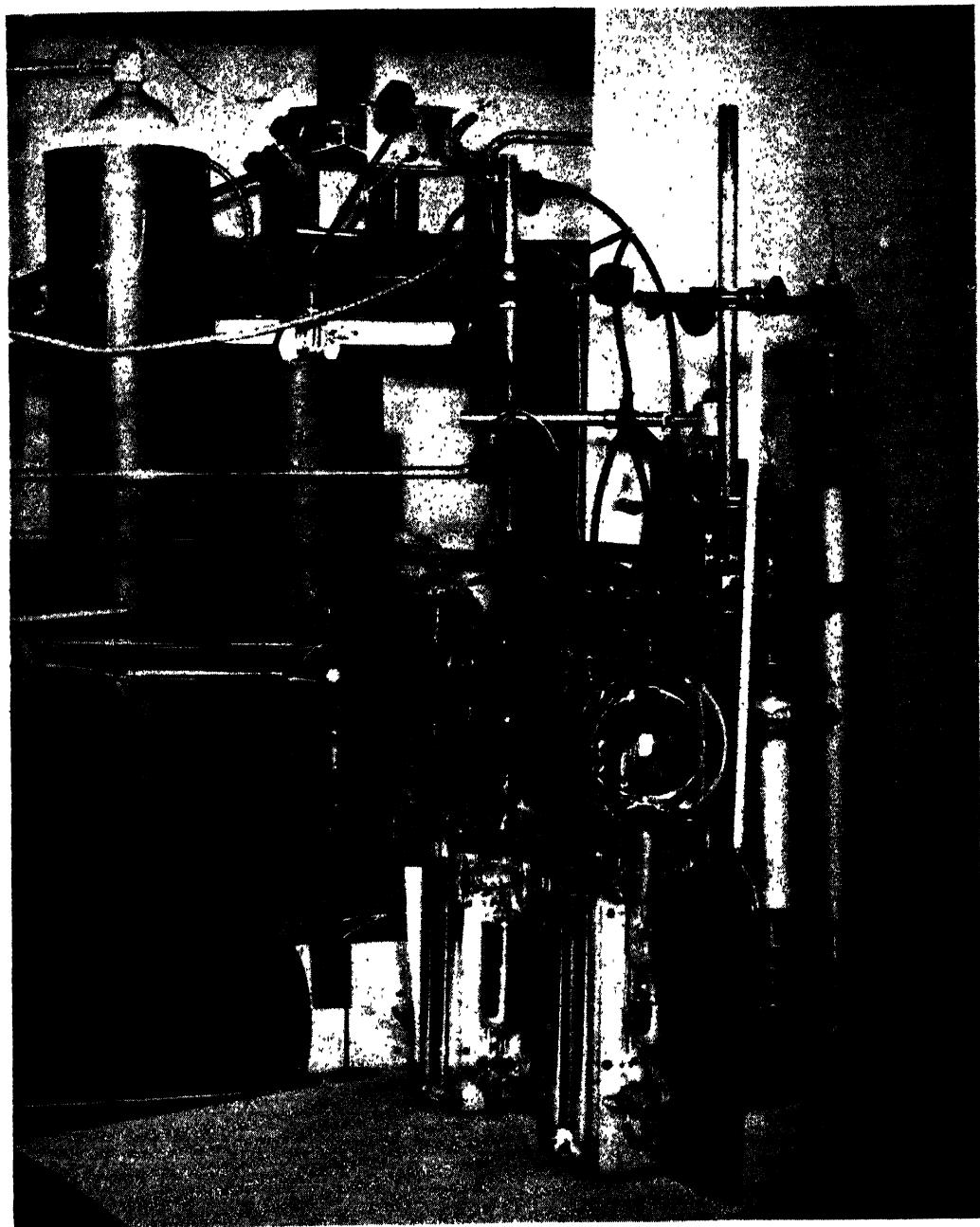


FIG. 5. The two unshielded counters seen on the right comprise a set of $1\frac{1}{2}$ in. diameter counters. The long and short 3 in. diameter counters are on the left and are shielded by lead.

To prove that the error due to any radius effect is less than that estimated above it is necessary to show that the counts per unit (cathode) volume in counters of approximately 0.5 in. and 3 in. diameter is not greatly different. On the basis of the rough calculation above, a difference of less than 5% should emerge if counts are lost only in a distance less than 0.2 mm. from the cathode.

An experiment was therefore carried out in which carbon dioxide containing C^{14} was admitted to the four small counters used in the determination of the half life of C^{14} .** The counts per unit volume in each of the two sets of compensated counters was determined and the pressure was noted. The results are shown in Table II. Owing to the fact that the volume of the 3-in. counters is considerably greater than that of the smaller counter units it was then necessary to expand a known fraction of the gas from the smaller to the larger counters in order to give a convenient counting rate. Inactive gas was then added to give a suitable total pressure. The complete results are shown in Table II.

TABLE II

Counter radius, cm.	Pressure of original active gas sample, cm. of Hg at 25° C.	Counts per unit volume, sec. ⁻¹ cm. ⁻³	Counts per unit volume corrected to 20 cm. of Hg at 25° C., sec. ⁻¹ cm. ⁻³
0.584	15.555	1.298	1.67
0.697	15.555	1.257	1.62
3.499	0.513	0.0432	1.68

From the results shown in the final column of Table II it is seen that the radius effect is certainly less than that calculated at the beginning of this section and that any correction arising from it is negligible.

A confirmatory experiment was also carried out by approximately doubling the pressure by adding inactive carbon dioxide and carbon disulphide in the long 1.384 cm. diameter counter. The counts with a filling of 10.17 cm. of mercury total pressure was 2.81 counts per second. Inactive gas was added to bring the total pressure up to 19.94 cm. of mercury. The counts observed were 2.82 per second. This is in agreement with the results obtained using external sources and inactive gas fillings. In these it was observed that the counting rate of the plateaux was the same over wide ranges of pressure when the geometry of the external Co^{60} source was unchanged (see Figs. 3 and 4).

Another kind of radius effect could, however, occur if such large counters showed a variation of efficiency as a function of radius due to some inherent property of the gas filling (e.g., loss of counts initiated in regions of low electric intensity remote from the wire). Such an effect should emerge from the experiment described above but an additional experiment was carried out with the apparatus illustrated in Fig. 6. In this apparatus a collimated beam of electrons could be directed into the counter in a direction parallel

** See preceding paper.

to the counter axis at different radii. The source used was Tl^{204} , which was prepared by irradiating a small piece of thallium metal in the pile. The resulting thallium activity was checked and found to have negligibly small

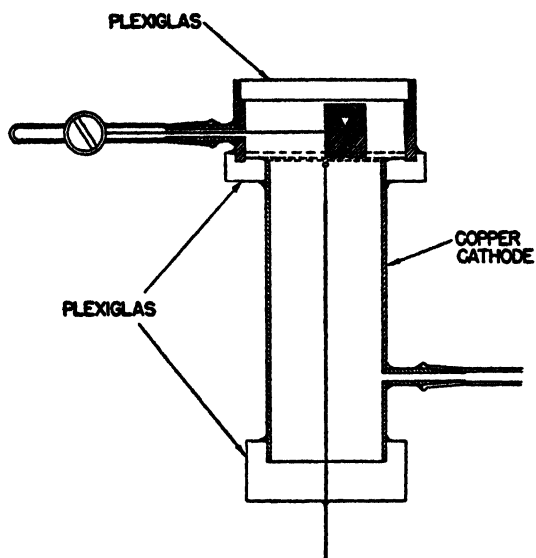


FIG. 6. Section through counter for determining radial efficiency.

gamma ray activity. The maximum energy of the beta particles from Tl^{204} is 1.6 Mev., which is considerably greater than that of those from C^{14} . If, however, there is no change in efficiency with radius using Tl^{204} then there should likewise be none with C^{14} since the specific ionization for the C^{14} beta particles is greater. As will be seen from Fig. 6 the geometry is such that only the beginning of the range of the Tl^{204} beta particles is utilized. The apparatus was designed in such a way as to avoid any kind of window, e.g., mica, so as to eliminate the possibility of spread of the beta particle beam due to scattering. The hole for collimation of the beta particles was 0.8 mm. diameter and 1 in. long. In interpreting the results a small allowance has to be made for the width of the electron beam.

The results obtained using argon at 10 cm. of mercury pressure and ethyl alcohol at 2 cm. of mercury pressure are shown in Fig. 7, in which an indication of the position of anode, anode bead, and cathode is given. Neglecting the extreme dip in the middle caused by absorption of beta particles in the glass bead and integrating for $2\pi Nr.dr$ across the counter an efficiency of 98.4% is obtained. This figure is based on the assumption that the flat part of the curve corresponds to 100% efficiency. This, in turn, is based on the criterion that, in the Geiger region, every particle entering the counter gives a count.

Similar results with the counter filled with carbon dioxide at 4.5 cm. of mercury pressure and carbon disulphide at 0.5 cm. of mercury pressure are included in Fig. 7 and show little over-all difference in efficiency from that for argon and alcohol. The region in the center of the counter gives an essentially

identical efficiency for both fillings. It is concluded therefore that the efficiency for the 6.998 cm. diameter counter is of the order of 98%.

The dotted lines in Fig. 7 indicate the geometry of the 1.167 cm. diameter counter. The thresholds of the 1.167 and 6.998 cm. diameter counters were

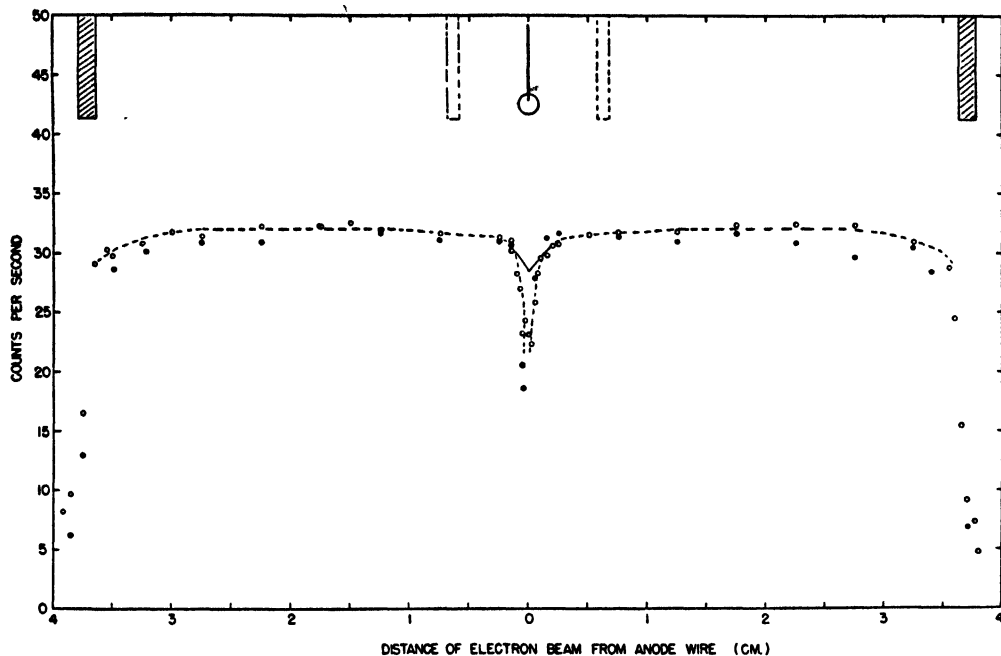


FIG. 7. Change of counting rate with radius. Solid points represent results for carbon dioxide and carbon disulphide. Open circles are results for argon and alcohol.

such as to give approximately the same intensity at the anode wire in each case, namely about 100,000 v. per cm. The distribution of electric intensity across the counter will be the same in both cases, being inversely proportional to radius and independent of cathode radius. It is assumed, therefore, that the variation in efficiency for the 1.167 cm. diameter counter near the anode wire will be the same as that determined for the larger counter. On integrating $2\pi Nr.dr$ up to a radius of 0.584 cm. an efficiency of 96.2% for the 1.167 cm. diameter counter is obtained.

This efficiency, however, is determined with a beam of electrons that is parallel to the anode wire, but in the determination of the C^{14} activity beta particles are emitted uniformly in all directions with an average range of about 9 cm. in carbon dioxide at a pressure of 20 cm. of mercury. The majority of the C^{14} beta particles will, wherever they originate, thus traverse a large region of the counter, creating one ion pair approximately every 0.2 mm. of path and at varying distances from the anode. The efficiency for these particles will therefore lie nearer to the efficiency (98.5%) at the cathode wall and will therefore probably be greater than 96.2%. An average value of 97% has therefore been assumed for the efficiency of the 1.167 cm. diameter counting unit for C^{14} beta particles.

Conclusion

The carbon dioxide and carbon disulphide counters used in the determination of the half life of C^{14} have been shown to be at least 97% efficient and of the same order as that for counters filled with mixtures of argon and alcohol.

Acknowledgments

We wish to thank Dr. W. B. Lewis for his helpful comments on reading this and the preceding paper and Dr. A. J. Cipriani for his ever-ready help in the procurement of equipment and the placing of laboratory and experimental facilities at our disposal. We wish again to thank Mr. F. N. MacGillivray for his assistance.

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THE CARBONYL GROUP IN BIRCH LIGNIN¹

BY ALAN BELL AND GEORGE F WRIGHT

Abstract

When lignin is extracted from birch wood with acetic acid its behavior differs from that of lignin extracted with acetic acid and then boiled with formic acid. There is less hydroxyl lost per methoxyl gained when the lignin treated with formic acid is methylated with diazomethane. An increase in addition of Grignard reagent also corresponds to this increase in methoxyl. This indicates that a lactone linkage is present in extracted lignin but probably not in lignin in the wood, because the effect is less noticeable in lignin more mildly extracted by acetic acid. In dimethyl sulphate - alkali-methylated lignins, where the lactone would no longer be present there is evidence of a carboxyl group which can be diazomethane-methylated and the resulting ester saponified at will.

The addition of Grignard reagent to lignins (about 1 equivalent per kilogram) has shown that a carbonyl group is present (4) in lignin which has been extracted from the wood by formic acid. Comparison of active hydrogen and Grignard reagent addition before and after diazomethane-methylation indicated the possibility that this carbonyl group was part of a lactone linkage (2), especially after it was found that diazomethane contaminated with methanol would react with a lactone (3). Further investigation using acetic acid as an extractant showed that the lactone group was probably not present in the wood, but was formed by the formic acid as a result of glucoside hydrolysis with subsequent lactonization of the resulting carboxyl group (1). In the present report a further evaluation of this hypothesis has been explored by combinations of diazomethane and dimethyl sulphate methylation studies on the lignins extracted from birch wood by both acetic and formic acids.

Reliable evidence has never been presented to show that lignin is a chemical individual, but heterogeneity in birch lignin is especially apparent in the fact that the methoxyl content differs in the several fractions into which it has been separated. Both the ether-soluble and the benzene-soluble fractions have the highest methoxyl content while the fractions soluble only in methanol and chloroform contain less methoxyl. Classification on the basis of methoxyl content of these original fractions is actually not justified because the methanol and chloroform fractions contain considerable carbohydrate. However, removal of the latter from the combined methanol and chloroform-soluble fractions with formic acid (to give acetic-formic lignins) allows separation of this lignin into a fraction soluble only in acetone-water, a fraction which is also soluble in acetone alone, and a fraction which is soluble in chloroform as well. It may be seen in Table I that, after the chemically linked carbohydrate has been removed, the fractions with limited solubility also contain less methoxyl groups than the ether and the benzene-soluble fractions (though they too must contain a small amount of carbohydrate). It may also be

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Contribution from the Chemical Laboratories, McGill University, Montreal, Que., and the University of Toronto, Toronto, Ont.

TABLE I
BIRCH LIGNINS METHYLATED WITH DIAZOMETHANE

Fraction and solubility	Initial OCH ₃ , %	Final OCH ₃ , %	Yield, wt. %	Grignard analyses in dioxane, per kgm.	
				Act. H	RMgX added
Acetic birch					
Ether	21.0	24.3	80	3.3	1.7
Benzene	20.7	23.1	90	3.5	3.0
Methanol	18.9	23.6	90	2.7	2.4
Chloroform	16.4	21.1	80	2.6	2.4
Acetic-formic birch					
Chloroform	22.1	27.9	90	3.3	2.5
Acetone	19.0	27.6	80	2.9	1.7
Acetone-water	17.8	27.2	80	2.2	2.4

observed that treatment with diazomethane raises the methoxyl values of all three of these acetic-formic fractions to the same level.

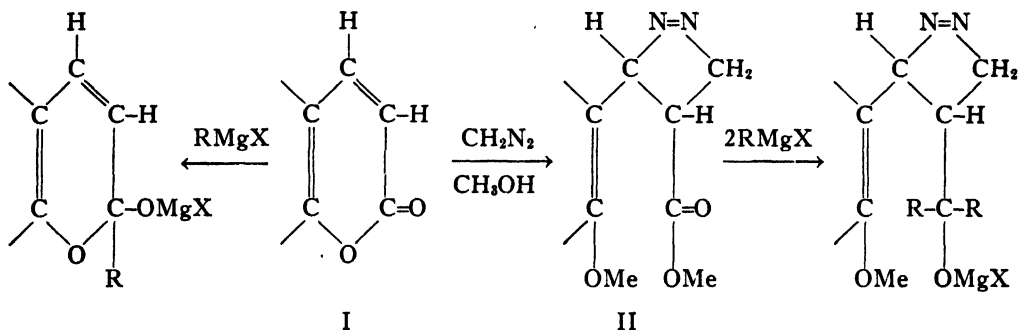
A critical comparison of the methoxyl and Grignard analyses with those for the original fractions has been outlined in Table II. This comparison discloses, first, that the methoxyl increase always is greater than the decrease in active hydrogen as measured in the Grignard machine. This abnormality is recorded in Column 4, Table II, as the difference between Columns 2 and 3.

TABLE II
COMPARISON OF "HYDROXYL LOST" TO "METHOXYL GAINED" IN REACTIONS OF ACETIC AND ACETIC-FORMIC LIGNINS WITH DIAZOMETHANE

(1) Lignin fraction and solubility	(2) Increase OCH ₃ /kgm.	(3) Loss, OH/kgm.	(4) Diff. 2-3	(5) Increase addn. RMgX/kgm.
Acetic birch				
Ether	1.2	0.6	0.6	0.8
Benzene	0.8	0.4	0.4	0.85
Methanol	1.7	1.0	0.7	0.65
Chloroform	1.7	0.4	1.3	0.5
Acetic-formic birch				
Chloroform	2.1	0.6	1.5	1.6
Acetone	3.2	0.4	2.8	1.0
Acetone-water	3.4	0.7	2.7	1.4

The table shows, secondly, that this diazomethane methylation causes an enhancement in the amount of Grignard reagent which can be added to the lignin, and this enhancement corresponds very roughly with the increase in methoxyl content (Column 5).

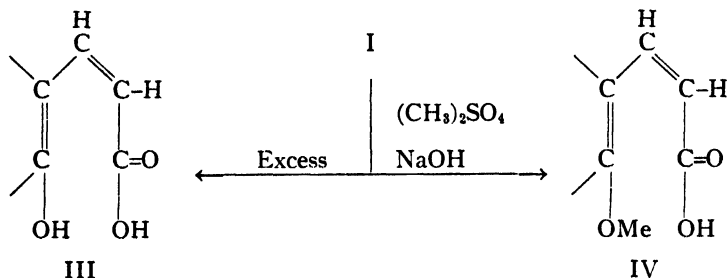
These results may be explained by the assumption that an α,β -unsaturated aromatic lactone such as I in lignin has been converted by methanolysis and reaction with diazomethane to the corresponding methoxymethyl ester, II. This has been illustrated as a coumarin type since coumarin has been found to behave in such a manner in a methanolic solution of diazomethane (3); but it is probable that other α,β -unsaturated lactones will act likewise.



Thus according to this formulation an increase in methoxyl content ought to be accompanied by an increase in additivity of Grignard reagent, without involving loss of active hydrogen. Table II shows this qualitatively to be true.

If this effect is indeed due to lactone formation following glycoside hydrolysis during extraction then the acetic formic lignin, which has lost most of its carbohydrate, should show a greater methoxyl increase and a greater Grignard addition than the corresponding acetic lignins after diazomethane-methylation. Table II shows this correspondence.

If this formulation expresses correctly the lignin structure with respect to its carboxyl groups, then methylation with dimethyl sulphate and alkali ought to convert I into the hydroxy acid, III, or the methoxy acid, IV, depending on the acidity of the enolic hydroxyl group.



The results of dimethyl sulphate + alkali-methylation of the various lignin fractions, which are recorded in Table III, tend to support the assumptions. The extent of methylation is, of course, much higher than that attained with diazomethane, since alcoholic and enolic hydroxyls will all be methylated by this reagent. Significantly, however, the lignin still contains free hydroxyl. Its ability to add Grignard reagent has actually decreased from that found

TABLE III
DIMETHYL SULPHATE METHYLATION OF BIRCH LIGNIN

Fraction and solubility	Amount used, gm.	Original OCH_3 , %	Yld., gm.	Final OCH_3 , %	Anal. for		Machine analysis in dioxane	
					C %	H %	Act. H/kgm.	RMgX added /kgm.
Acetic birch								
Ether	1.5	21.0	1.1	34.6	64.6	6.1	1.8	0.9
Benzene	1.8	20.7	1.3	35.0	64.3	6.4	1.7	0.8
Methanol	1.8	18.9	1.4	35.4			1.7	0.8
Chloroform	1.7	16.4	1.3	35.0			1.8	0.7
Acetic-formic birch								
Chloroform	1.2	22.1	1.0	35.8	66.3	6.1	1.6	1.4

for a comparable diazomethane-methylated lignin. This might be expected if ester linkages had been hydrolyzed by the action of the alkali to leave the salts of free carboxyl groups.

Inspection of Table III shows the interesting phenomenon that all fractions have been methylated to about the same OCH_3 content. The carbohydrate originally present in the less soluble fractions has evidently been hydrolyzed during the repeated alkali treatment, because the methoxyl value does not change after treatment with boiling formic acid. But the less soluble fractions originally contained less methoxyl, even on the carbohydrate-free basis. This would indicate that dimethyl sulphate + alkali had converted these less soluble fractions to the chemical equivalent of the more soluble fractions.

These fractions which have been methylated with dimethyl sulphate and alkali are for the most part not completely soluble in aqueous alkali unless much dioxane is added. Indeed they behave as would be expected of a substance of high molecular weight with insufficient hydrophilic groups (such as carboxyl) to effect complete solution. Thus they tend to retain sodium as the salt unless they are strongly acidified.

One of the repeatedly methylated ether + benzene-soluble fractions is, however, completely soluble in the alkaline reaction mixture resulting from treatment with dimethyl sulphate; but after acidification it cannot again be dissolved in the same dilute alkali. A higher concentration over a long period of time is required for solution. It would appear that, in this case, acidification permitted a reversal of the process I \rightarrow III and involved re-formation of a lactone.

As might be expected, this fraction (presumably lactonized) increased in methoxyl content from 34.3 to 39.6% when treated with diazomethane, and no decrease was discovered in active hydrogen content. An increase in addition of Grignard reagent was observed which would be expected if I were

converted to II. Further confirmation that diazomethane effected esterification was obtained by saponification with alkali, which reduced the methoxyl content to 33.9%.

The methoxyl content of another, less soluble, fraction (34.0% OCH_3 after dimethyl sulphate-methylation) was increased only to 36.8% by treatment with diazomethane, but the original methoxyl content was restored by alkaline saponification. It may be seen that the differential in methoxyl content is not so great as is the case with the more soluble fractions. This is not unexpected when it is realized that lignin is a complex mixture (not a single compound) and therefore that its chemistry will be qualitatively but not quantitatively exact.

On the basis of these results it is suggested that a carboxyl group with a tendency toward lactonization is present in birch formic or acetic lignin to the extent of less than 1 group per kilogram of lignin.

Experimental

Diazomethane-methylation

The procedure outlined previously (4) was employed, using the diazomethane from 2.5 cc. of nitrosomethylurethane per gram of lignin, in 50 cc. of dioxane. This diazomethane was contaminated with the methanol used in its preparation. Analytical samples of the methylated lignin were prepared by precipitation of dioxane solutions into 10 volumes of petroleum ether (b.p. 40° to 60°). Yields and analyses are shown in Table I.

Dimethyl Sulphate + Alkali-methylation

The method outlined previously (2) was employed with the variation that dioxane instead of acetone was used as the organic solvent. The products, after four treatments with dimethyl sulphate and 30% aqueous sodium hydroxide under nitrogen (reaction distinctly alkaline when reaction complete), were acidified, dissolved in chloroform, and precipitated into petroleum ether (b.p. 40° to 60°). The yields and properties are shown in Table III.

Lactone Nature of More Soluble Fraction

A chloroform solution of 10.5 gm. of dimethyl sulphate+alkali-methylated ether-benzene soluble fraction (OCH_3 , 34.0%) was washed with 1% aqueous sodium hydroxide to remove an alkali-soluble fraction (isolated by acidification of the alkaline extract; wt. 0.78 gm., methoxyl 25.7%). The alkali-insoluble remainder in the chloroform was evaporated to dryness, redissolved in 400 cc. of dioxane, and stirred under nitrogen while 50 cc. of dimethyl sulphate and 150 cc. of 30% aqueous sodium hydroxide were added over an eight hour period. The dioxane layer was separated and poured into 1800 cc. of water to give a *clear* solution. Upon acidification with hydrochloric acid, a precipitate appeared which was taken up in chloroform. The latter solution, after

evaporation to 150 cc. (20 mm.) was filtered and precipitated into 1500 cc. of petroleum ether (b.p. 40° to 60°). It weighed 7.0 gm., methoxyl 34.3%. It was now again insoluble in 1% aqueous sodium hydroxide. In the Grignard machine, this sample gave 2.2 active hydrogen and 0.6 RMgX added per kgm.; in pyridine it gave 2.7 active hydrogen and 1.6 RMgX added.

Esterification of Dimethyl Sulphate-Methoxylated Ether-benzene Soluble Fraction

A solution of 7.0 gm. (OCH_3 , 34.3%) of this fraction in 280 cc. of dioxane was treated for three days with a diazomethane solution prepared from 10 cc. of nitrosomethylurethane. After vacuum evaporation the lignin was dissolved in benzene and precipitated into 10 volumes of petroleum ether (b.p. 40° to 60°). Weight 5.6 gm.; OCH_3 , 39.6%; Grignard analysis per kgm.: in dioxane 2.4 active H, 1.0 RMgX added; in pyridine, 2.5 active H, 1.1 RMgX added. The centrifuge liquors from this precipitation were evaporated to dryness. The residue in ether was precipitated into petroleum ether (weight, 0.14 gm., OCH_3 , 41.3%).

When 0.4 gm. of the material with 39.6% OCH_3 was dissolved in 25 cc. benzene and boiled 10 hr. with 30 cc. of 5% hydrochloric acid, 0.34 gm. was recovered by precipitation into petroleum ether, OCH_3 , 36.5%.

A 0.3 gm. portion of the material containing 39.6% OCH_3 was allowed to stand two days in a water-dioxane solution of 5% sodium hydroxide. After dilution into water, the precipitate was dissolved in chloroform and reprecipitated into petroleum ether. The 0.25 gm. which was recovered contained sodium and 32.9% OCH_3 . After re-solution in chloroform, it was washed with dilute hydrochloric acid and again precipitated to give a methoxyl value of 33.6% and no sodium.

Dimethyl Sulphate-methylated, Chloroform-methanol Soluble, Fraction

1. Esterification

When 3 gm. of this fraction (OCH_3 , 34.0%) was treated with diazomethane solution for three days, precipitation from benzene into petroleum ether yielded 2.8 gm., methoxyl 36.8%. Grignard analysis in dioxane, per kgm.: 1.5 active H, 1.2 RMgX added.

When this material was saponified by treating a solution in 5 cc. of dioxane with 2 cc. of 5% aqueous sodium hydroxide at 20° C. for 24 hr., the methoxyl content of the acidified reaction product was 34.0% after precipitation from benzene into petroleum ether.

2. Action of Formic or Acetic Acids

One gram portions of this fraction (OCH_3 , 34.0%) were refluxed for 12 hr. with each of these solvents. The product from acetic acid treatment was 1 gm. of material unchanged in methoxyl (34.0%). After treatment with 95% formic acid 0.90 gm. (OCH_3 , 34.4%) was recovered.

Acknowledgment

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THE ISOBUTYL GROUP IN SPRUCE AND BIRCH LIGNINS¹

BY ALAN BELL AND GEORGE F WRIGHT

Abstract

Acetone has been isolated by permanganate oxidation of birch and spruce lignins extracted from wood by acetic or formic acid. Acetone was obtained also when the formic acid lignins were ozonized but not from the acetic acid-extracted lignins. This difference was confirmed when perbenzoic acid titration indicated unsaturation in the formic acid extract which was not present in the acetic acid extract. It is suggested that an α -hydroxy- β -methoxyisobutyl group is present in lignin; during acetic acid extraction the hydroxyl group is acetylated but during formic acid extraction the formic acid reduces the group to isobutenyl, which will give acetone when it is ozonized.

In a brief communication (2) it was announced that acetone had been isolated as an oxidation product of formic acid spruce lignin (9, 11). This oxidation has now been repeated with formic acid spruce as well as with formic acid birch (6) and acetic acid (3) birch lignin. In order to insure that the acetone did not arise from carbohydrate these lignins were first boiled with aqueous 25% *p*-toluenesulphonic acid. The three carbohydrate-free lignins were then oxidized with alkaline potassium permanganate to yield 0.4%, 0.7%, and 0.5% respectively of acetone, determined as the 2,4-dinitrophenylhydrazones.

Thus evidence is at hand that all of these lignins contain the isopropyl group. However, ozonization of these isolated lignins yielded acetone only when the lignins had been isolated from the wood with boiling formic acid (Table I). This extraction agent must therefore react with the lignin to form an isopropylidene radical whereas the acetic acid extraction yields a saturated isopropyl group.

It will be observed (Table I) that less than half of the lignin is destroyed by ozonization, the remainder being recovered as water-soluble and water-insoluble lignin-like products. The former predominate when the ozonization is more complete. From the lignin-like nature of these products it would seem that the essential nucleus is still intact. Only substituent fragments (containing, however, most of the methoxyl content) seem to have been affected by ozone. The remainder, containing about 5% OCH_3 , would appear to have been split at two positions per kilogram of lignin, because the addition of Grignard reagent in pyridine, which is doubled by diazomethane methylation, indicates four carboxyl groups per kilogram of water-soluble ozonization product. This water-soluble product is being investigated in a further study of lignin ozonization.

The presence of an ethylene linkage in formic acid lignins, which was absent in the corresponding acetic acid lignins, was thus demonstrated through

¹ Manuscript received February 15, 1949.

Contribution from the Chemical Laboratories, McGill University, Montreal, Que., and the University of Toronto, Toronto, Ont.

TABLE
OZONIZATION OF LIGNIN

Before ozonization				After ozonization								
Expt.	Type of lignin	Wt. used, gm.	OCH ₃ in isolated lignin, %	Acetone derivative	Acetone, wt. %	Oxalic acid, wt. %	Water-insoluble		Water-soluble; acetone-ether-insoluble		Water-soluble; acetone-pet. ether-insoluble*	
							Wt., gm.	OCH ₃ , %	Wt., gm.	OCH ₃ , %	Wt., gm.	OCH ₃ , %
1	Methylated acetone-sol., formic birch	10	15.7	0.85 gm. acetone superoxide	6.6		5.0	6.2	2.5			
2	Chloroform-soluble formic birch	10	19.6	0.34 gm. benzal-acetone	1.4	4.2			3.3 4.35	5.4 3.7	2.5 0.9	6.1 4.6
3	Chloroform-soluble formic spruce	1	11.7	0.06 gm. acetone superoxide	4.8		0.15					
4	Unfractionated acetic birch	10	17.6	None	None	3.0	0.25		4.5			
5	Methanol-soluble acetic birch	10	14.7	None	None	3.0	0.8		5.7			
6	Unfractionated acetic formic birch, acetylated	10	19.7	None	None	3.1	3.0		1.0			

* Skellysolve F was the petroleum ether used in the precipitations.

ozonization by the preparation of suitable derivatives of acetone. The extent of this unsaturation could not, however, be evaluated by ozonization because of considerable variability in yield. The amount of ethylenic linkage was therefore estimated by perbenzoic acid titration at 0° C. Within two hours the formic acid lignin consumed 0.6 equivalent more of perbenzoic acid than did the acetic acid lignin, and this difference in consumption prevailed during the slow disappearance of the oxidizing agent over 10 days.

In order to ascertain the mechanism of formation of this additional double bond during the extraction process with formic acid, a comparison of the various birch lignin fractions must be made. Both the benzene-soluble and the benzene-insoluble fractions have been examined for methoxyl, acetyl, or formyl, and for hydroxyl content (Zerewitinoff).

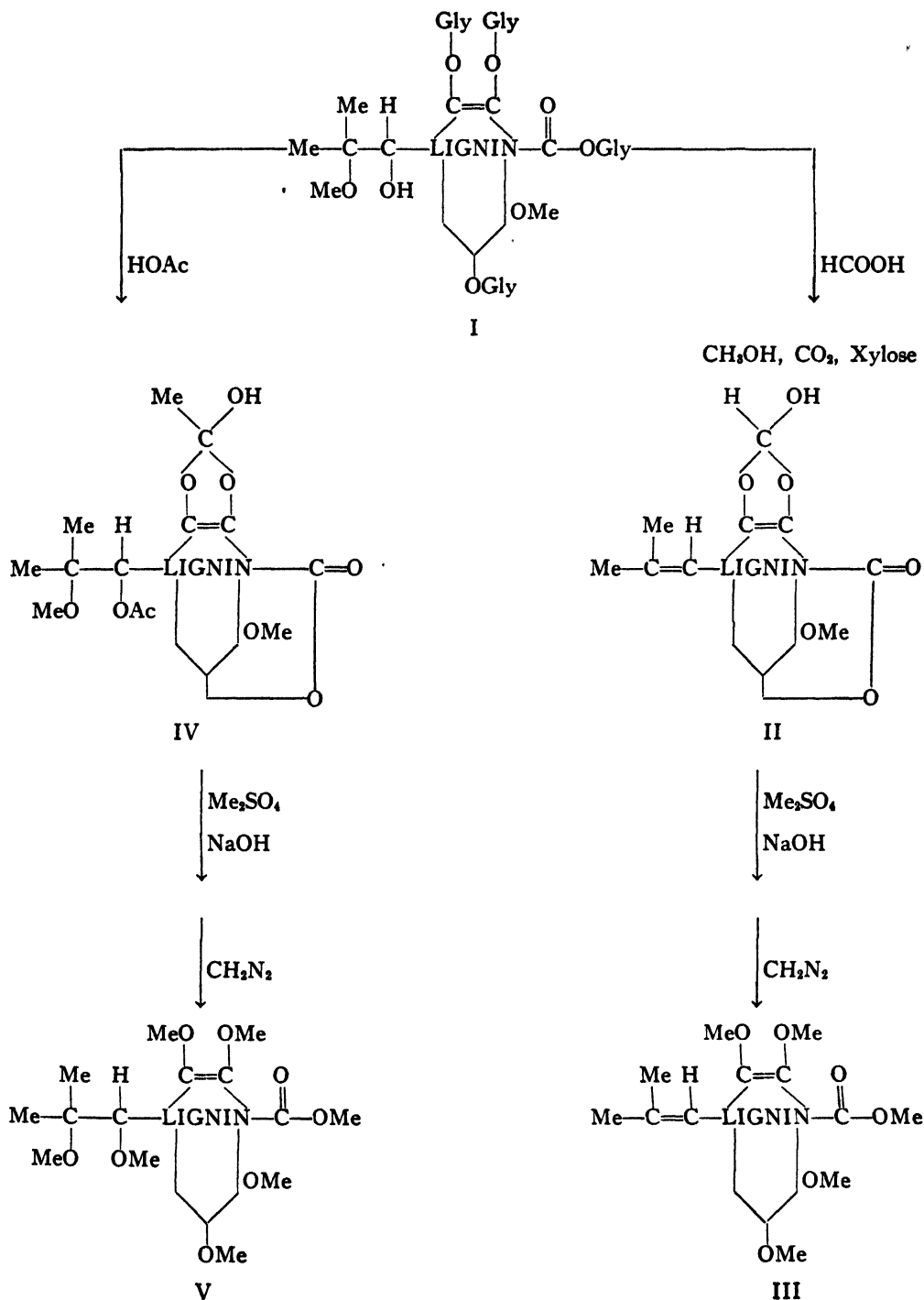
TABLE II

METHOXYL AND ACTIVE HYDROGEN CONTENTS OF ACETIC, FORMIC, AND ACETIC-FORMIC LIGNINS

Type and fraction of lignin	Methoxyl groups per kgm., ester and carbohydrate-free basis	Hydroxyl groups per kgm. (Grignard active H in pyridine)	Ester content		Total free esterified hydroxyl groups per kgm.
			Acetyl groups per kgm.	Formyl groups per kgm.	
Acetic					
Benzene-sol.*	7.6	8.4	0		8.4
Benzene-insol.	6.3	7.9	0.5		8.4
Formic					
Benzene-sol.	7.0	5.7		1.1	6.8
Benzene-insol.	5.7	6.7		0.8	7.5
Acetic formic					
Benzene-sol.	7.7	6.1	1.2		7.3
Benzene-insol.	6.2	7.7	1.1		8.8

* This lignin had been saponified with sodium hydroxide.

Data in Table II compiled from previous studies of these acetic (3) and formic (6) lignins show that, as compared with acetic acid extract, the formic birch lignins have lost both methoxyl groups and active hydrogen during the extraction from wood. However, when the acetic acid extract is *subsequently* treated with boiling formic acid, no methoxyl loss and very little loss in active hydrogen (hydroxyl groups) is noted. This would indicate that treatment with acetic acid has blocked groups with which the formic acid could otherwise react. On the basis of acetate-ester content, such blocked groups should have been hydroxyl. This evidence may be interpreted by a formulation which depicts the known characteristics of acetic and formic birch lignins.



This formulation represents lignin in wood as I, with phenolic, ene-diolic, and carboxylic (3, 4) hydroxyls presumably bound to the wood polysaccharide glycosidically. The extraction with formic acid to give formic acid birch lignin, II, has previously been assumed not only to break the glycosidic linkages

but also to form a 2-hydroxy-1,3-dioxole ring. This hemi-orthoester formation at the ene-diolic linkage is postulated to account for the introduction of two methoxyl groups by diazomethane treatment of a saponified formic acid lignin where only one hydroxyl group was indicated by Grignard analysis before saponification. It has also been assumed (3) that the carboxyl group when freed from its glycosidic bonding forms a coumarin-type of lactone (8). Finally the present research indicates a 1-hydroxy-2-methoxyisobutyl radical in natural lignin, I, which is converted by formic acid into the isobutenyl group shown in II. This ethene formation is remindful of the conversion of glycerol to allyl alcohol (10) and may also involve an orthoformate intermediate (7). Eventual methylation of II will then give III.

Extraction of wood by acetic acid, on the other hand, will give the acetic birch lignin, IV, containing the 1-acetoxy-2-methoxyisobutyl group; the lateral methoxyl is retained and the lateral hydroxyl group in I is acetylated because acetic, unlike formic acid, would not convert a 1,2-glycol to an ethene. Eventual methylation of IV will thus give V, somewhat richer in methoxyl than III.

According to this concept, formic acid birch lignin II differs from acetic acid birch lignin IV by containing 0.6 double bond instead of 0.6 methoxyl and 0.6 acetoxy group per kgm. of lignin. A corresponding difference of 1.2 methoxyl group per kgm. should then appear when these lignins are completely methylated with respect to dimethyl sulphate and diazomethane. Actually, the difference in the completely methylated lignins between the acetic fraction A (OCH_3 , 39.6%) and the formic fraction A (OCH_3 , 34.8%) is approximately the same as between the acetic fraction B (OCH_3 , 36.6%), (V), and the formic fraction B (OCH_3 , 32.3%), (III), namely 1.4 to 1.5 methoxyl groups per kgm. It is evident therefore from the methoxyl values that the acetic acid lignin has more hydroxyl function available for methylation than has the formic acid lignin, although the difference is greater (by 0.3 group per kgm.) than was expected from the perbenzoic titrations. This discrepancy may be owing to the titration (ozonolysis gave a higher acetone value, but it is difficult to dry acetone superoxide). However, it is more likely to be owing to incomplete recovery from the methylation of a nonhomogeneous material such as lignin, and from faults arising in the methoxyl determination of lignins (1).

Experimental

Ozonization of Lignins

The solvent, chloroform, was washed with concentrated sulphuric acid, then with 10% potassium hydroxide, dried with calcium chloride, then treated with ozone for several hours, finally washed with dilute hydrochloric acid followed by continuous water washing for 12 hr. One hundred cubic centimeters of the dried, distilled solvent was used per gram of lignin. In case the lignin was not chloroform-soluble, either methylation (Table I, Expt. 1) or acetylation (Expt. 6) conferred on the lignin the requisite solubility. The solution was chilled with an iced water bath, and dry oxygen containing 12%

ozone was passed through until analysis of the effluent gases showed that no more ozone was being absorbed.

The resulting solution, bleached from a dark red to a turbid light yellow color, was evaporated at 35° to 40° C. (15 mm.), leaving a yellowish-white residue. If the latter was treated with 26 cc. of 1% hydrogen peroxide for 12 hr., followed by 30 min. reflux, acetone superoxide was obtained on steam distillation. If water rather than hydrogen peroxide were used for this treatment, acetone was isolated as an aqueous distillate (water being added during the distillation). The acetone in this aqueous distillate was isolated either as the 2,4-dinitrophenylhydrazone (m.p. 125° to 128° C.), or as dibenzalacetone (m.p. 108° C.) by treating the alkaline solution with an excess of benzaldehyde. Mixed melting points served to identify both substances. In the recorded experiment (Table I, No. 2) the benzalacetone isolated required an excess of acetone; the yield is therefore not significant.

The water-insoluble lignin material (sodium bicarbonate-soluble) was filtered off. The amount of this varied inversely with the completeness of ozonization and contained 6 to 8% methoxyl. Upon diazomethane methylation of the material (Table I, Expt. 1), this methoxyl was increased to 21.2%; Grignard analysis, 4.2 active H and 1.9 RMgX added per kgm. in dioxane.

The solution from which the water-insoluble material was filtered was now extracted continuously with ether for three days. When the ozonized material had been treated with hydrogen peroxide, the residue obtained by evaporation of the ether yielded acetone superoxide upon sublimation at 40° to 50° C. (10 mm.). After sublimation at this temperature was complete, an increase to 100° to 120° C. (10 mm.) yielded oxalic acid. Both substances were identified by mixed melting point with authentic samples.

The aqueous solution, following continuous ether extraction, was evaporated to dryness at 15 mm. (much foaming). The residue was dissolved in acetone and precipitated into ether to yield water-soluble lignin-like material containing 3.5 to 5.5% methoxyl. The ethereal centrifuge liquors contained a lignin-like material which was difficult to reprecipitate into petroleum ether (Skellysolve F) because of contamination with oxalic acid.

A weight of 4.35 gm. of this water-soluble lignin was obtained (Table I, Expt. 2). In the Grignard machine in dioxane this material gave 4.5 active H and 0.6 RMgX added per kgm.; in pyridine 9.3 active H and 4.4 RMgX added per kgm. After two treatments with diazomethane, the methoxyl value was increased to 20.6%; Grignard analysis in dioxane, 3.5 active H and 1.4 RMgX added per kgm.; in pyridine 9.2 active H and 9.7 RMgX added per kgm.

Oxidation of Lignins with Alkaline Permanganate

The lignin was first freed from carbohydrate by boiling with aqueous *p*-toluenesulphonic acid. In a typical experiment, 8.5 gm. of acetone-soluble spruce lignin (9) (OCH₃, 12.7%; HCO, 3.5%) was heated to 100° C. with 500 cc. of 25% *p*-toluenesulphonic acid for four hours. The hydrolyzed mixture was then distilled at 15 mm. from a Claisen flask totally immersed in

a water bath, the side arm being filled with glass wool. When the water bath temperature reached 100° C. and the residue was completely dry, 200 cc. of water was added and the distillation process repeated. The distillate was neutralized with alkali and redistilled to remove 0.07% formaldehyde, determined as the dimedone derivative. The residual sodium salts gave strong tests for formate (5) but no trace of acetate could be detected by treatment of the sodium salt with *p*-nitrobenzyl chloride.

The de-formylated lignin was a black mass which was still soluble in dilute sodium hydroxide. It was washed until neutral to Congo red paper to eliminate *p*-toluenesulphonic acid; incidentally, soluble carbohydrate should also be removed by this treatment. The washed lignin was dissolved in 520 cc. of 0.4% sodium hydroxide and stirred at room temperature while 67 gm. of potassium permanganate was added over a three-day period. The flask was then fitted with an antifoaming device and stirred while 200 cc. was distilled over. This aqueous distillate was boiled 10 min. with 0.5 gm. of 2,4-dinitrophenylhydrazine, concentrated hydrochloric acid being added through the reflux condenser. After cooling, the solution was extracted four times with acetone-free chloroform. The latter solution was evaporated to dryness and freed from unchanged 2,4-dinitrophenylhydrazine by extraction with a *minimum* quantity of chloroform. Evaporation of this chloroform solution left 0.15 gm. of acetone 2,4-dinitrophenylhydrazone, m.p. 122° C., purified by crystallization from ethanol-dilute hydrochloric acid, m.p. 126° to 127° C., not lowered by mixed melting point. This corresponds to a 0.4% weight yield of acetone.

The residual oxidation product was treated with sulphur dioxide to dissolve manganese dioxide. The acidified solution was continuously extracted with ether; the residue upon evaporation of the ether extract was sublimed at 120° C. (10 mm.) to give a sublimate from which, by extraction with benzene, 0.01 gm. of succinic anhydride, m.p. 115° to 116° C., was obtained and identified by mixed melting point of the resublimed product, m.p. 118.5° C., with an authentic sample. The benzene-insoluble sublimate was soluble in acetone; it sublimed at 240° C. (760 mm.) and melted above 270° C.

An identical procedure with unfractionated acetic birch lignin (OCH₃, 17.0%) yielded 0.18% formaldehyde and 0.5% acetone. Formic birch lignin (acetone-soluble, OCH₃, 21%) under similar conditions for oxidation gave 0.7% acetone.

Perbenzoic Acid Oxidation of Lignins

One gram of chloroform-soluble formic birch lignin (OCH₃, 20.1%) dissolved in chloroform was cooled to 0° C. and diluted to a definite volume with a cold solution of perbenzoic acid (0.065 mole per liter) in chloroform. The reaction was maintained at 0° C., while 1 cc. portions were withdrawn at intervals and transferred to 20 cc. of water in a 100 cc. distilling flask. The chloroform in the aliquot was removed by evaporation under 20 mm. at room temperature and the residual solution treated with 2 cc. of 5% potassium

iodide and 3 cc. of 12% hydrochloric acid and titrated slowly and with difficulty using *N*/100 sodium thiosulphate and 10 to 15 drops of 0.2% starch solution.

This procedure was repeated with ether-soluble acetic birch lignin (OCH_3 , 19.2%). Comparison of the titration values shows that the formic acid lignin rapidly consumed 0.6 equivalent of perbenzoic acid per kgm. more than the acetic acid lignin, after which the rates of perbenzoic acid disappearance were equal over 10 days at 0° C.

TABLE III

TITRATION OF LIGNIN - PERBENZOIC ACID SYSTEM, ML. *N*/100 THIOSULPHATE
Reaction time, min.

Lignin type	0	400	4000	8000	16,000
Formic acid	6.50	5.82	4.63	4.09	3.25
Acetic acid	6.50	6.10	4.93	4.38	3.58

When the titration of aliquots indicated that the reaction was complete, the solutions, which were much lighter in color following the treatment with perbenzoic acid, were washed with 10% sodium thiosulphate followed by sodium hydroxide solution. Following a subsequent wash with 1% hydrochloric acid, the chloroform layer was evaporated at 20 mm. pressure. The residue was fractionated according to solubilities in benzene, chloroform, or dioxane. Because of the light color of the solution, the optical rotation was measured for a number of these samples; found $[\alpha]_{6563}^{26}$, -3° to -5° in chloroform.

Acknowledgment

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THE ULTRAVIOLET ABSORPTION SPECTRA OF NITRIC ACID SOLUTIONS¹

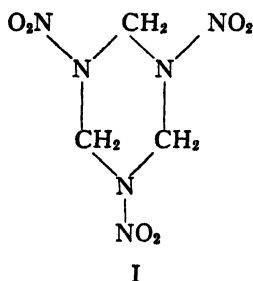
BY R. NORMAN JONES AND G. DENIS THORN

Abstract

The ultraviolet absorption spectra of binary mixtures of nitric acid, water, acetic acid, acetic anhydride, and nitrogen pentoxide have been investigated over the ranges of concentration in which the systems exhibit sufficient chemical stability. The variations in the spectra are considered in relation to the other physical properties of the systems, as reported in the literature. The ultraviolet spectrum of nitric acid in the presence both of nitrogen pentoxide and water is interpreted in terms of a series of equilibria which involve the nitrate (NO_3^-) and nitronium (NO_2^+) ions and associated and nonassociated neutral molecules. The specific gravities of anhydrous nitric acid solutions of ammonium nitrate, potassium nitrate, ammonium acetate, acetic acid at $20 \pm 0.1^\circ \text{C}$. and of nitrogen pentoxide at $25 \pm 0.1^\circ \text{C}$. are also reported.

Introduction

The explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (I), commonly known as RDX, is manufactured by two processes. In the "Direct" process, hexamine (hexamethylenetetramine) is nitrated with a large excess of nitric



acid of 97.5 to 99.5% concentration by weight. In the "Combination" or "Bachmann" process a solution of hexamine in glacial acetic acid is mixed simultaneously with acetic anhydride and with a solution of ammonium nitrate in nitric acid. Considerable research has been carried out on the mechanisms of these nitration reactions. In the case of the Combination process there are reasons to believe that the reaction is one of considerable complexity, and the yields of RDX are highly sensitive to small variations in the conditions of the reaction and the composition of the reaction mixture. In the simpler Direct process the yields also vary considerably with the strength of the nitric acid.

In an attempt to gain information about the mechanism of nitration of hexamine under the conditions operative both in the Direct and Combination

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processes, an investigation has been made of the ultraviolet absorption spectra of the individual reagents concerned in these processes, and of such binary mixtures of these reagents as are sufficiently stable at room temperature to allow of their spectrographic measurement.

The systems investigated are summarized in Table I, and are considered separately in the succeeding sections of the paper. There follows a general

TABLE I
SYSTEMS EXAMINED

System	Concentration*
A. Ammonium nitrate - water	0-80% ammonium nitrate
B. Nitric acid - water	0-20% water
C. Nitric acid - ammonium nitrate	0-54% ammonium nitrate
D. Nitric acid - potassium nitrate	0-25% potassium nitrate
E. Nitric acid - ammonium acetate	0-30% ammonium acetate
F. Nitric acid - acetic acid	0-80% acetic acid
G. Nitrogen pentoxide - acetic acid	0.054 molar with respect to nitrogen pentoxide
H. Nitrogen pentoxide - acetic anhydride	4.79 molar with respect to nitrogen pentoxide
I. Nitrogen pentoxide - carbon tetrachloride	0.282 and 0.102 molar with respect to nitrogen pentoxide
J. Nitric acid - nitrogen pentoxide	0-24% nitrogen pentoxide
K. Nitric acid - acetic anhydride	0-12 and 94-100% acetic anhydride

* *Per cent composition by weight unless otherwise indicated.*

discussion, and a section devoted to a description of the experimental techniques which were developed for the measurement of the spectra of thin films of highly corrosive materials. The general conclusions have been presented in a preliminary report (31).

A. Ammonium Nitrate - Water

Although no record of the ultraviolet absorption spectrum of aqueous solutions of ammonium nitrate has been found in the literature, the absorption is similar to that of solutions of the nitrates of the alkali metals. Hartley (25, 26) in 1902 measured the absorption spectra of aqueous solutions of several metallic nitrate salts, and observed a broad band in the region of 3020 Å; the position and intensity of this band varied only slightly with change in the cation, and he attributed it to the nitrate ion. In 1909, Baly, Burke, and Marsden (1) determined the spectra of alcoholic solutions of various nitrates and of nitric acid, and confirmed Hartley's observation that the band near 3020 Å is caused by the nitrate ion. Schaefer (41, 42) in 1915 observed that alkyl nitrate esters, unlike the nitrate salts, did not exhibit the 3020 Å absorption band; their spectra showed only "end absorption" with

no maxima detectable in the measured region of the spectrum (compare Fig. 1). Scheibe (44), Hantzsch (22) and von Halban and Eisenbrand (16, 17, 19) have measured the absorption spectra of sodium and potassium nitrates in the presence of various salt solutions, and have noted that the

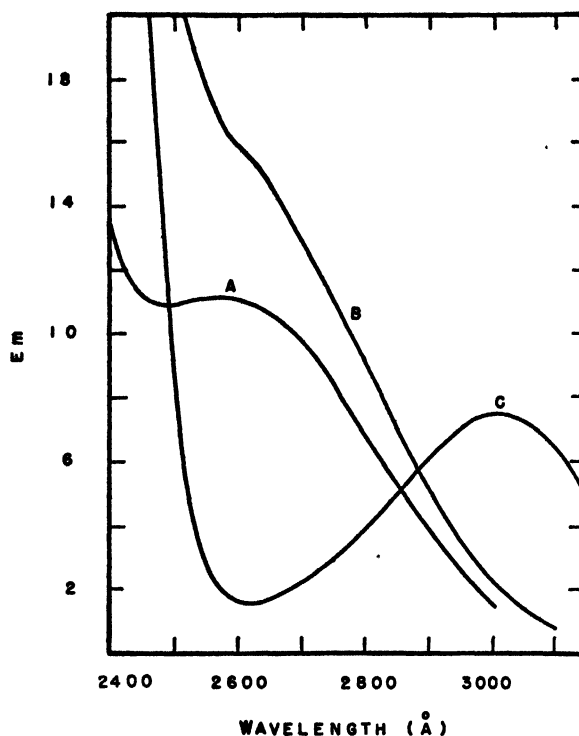


FIG. 1. Ultraviolet absorption spectra.

Curve A. Anhydrous nitric acid.

Curve B. Ethyl nitrate.

Curve C. Aqueous solution of ammonium nitrate.

molar extinction coefficient of the nitrate ion maximum at 3020 Å falls in intensity with increase in the concentration of the secondary electrolyte, while a new maximum appears at shorter wave lengths. Hantzsch (22) attributed these changes to solvation effects.

Experimental Observations

In these laboratories the absorption spectra of aqueous solutions containing from 0.99 to 805.4 gm. of ammonium nitrate per liter of solution have been measured. Over this concentration range the position of the maximum remains constant at 3015 Å (Fig. 1. Curve C); the molecular extinction coefficient at the maximum ($E_{m_{max}}$) changes only slightly, falling from 7.6 for dilute solutions to 6.9 for the most concentrated solution (see Table II). This absorption maximum can, without doubt, be attributed to the nitrate ion, and it may be inferred from the data in Table II that aqueous solutions of ammonium nitrate undergo little change in ionic condition as the concentration increases.

TABLE II
ABSORPTION OF AQUEOUS AMMONIUM NITRATE. INTENSITY AT THE MAXIMUM

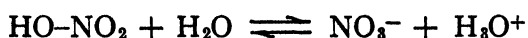
Concentration, gm./liter	$\log \frac{I_0}{I}$	Depth of solution, mm.	E_m at 3015 Å
0.99	0.094	10.00	7.5
2.99	0.279		7.5
3.32	0.316		7.6
4.67	0.433		7.4
5.53	0.517		7.5
10.83	0.107	1.06	7.4
20.01	0.196		7.5
30.30	0.306		7.6
40.07	0.397		7.5
	0.043	0.114	7.5
100.81	0.116		7.4
150.2	0.156		7.3
250.9	0.251		7.0
276.1	0.275		7.0
330.9	0.330		6.9
396.7	0.395		7.0
517.1	0.524		7.1
	0.090	0.0196	7.1
805.4	0.136		6.9

B. Nitric Acid - Water

The ultraviolet absorption spectrum of nitric acid has received extensive study from several investigators. The spectra of dilute solutions of nitric acid are similar to those of the alkali nitrates (1, 17, 18, 19, 22, 26, 33, 37, 41) but changes occur as the concentration of the nitric acid is increased. Hartley (26) noted that the nitrate ion absorption band near 3020 Å disappeared with increase in the nitric acid concentration. Schaefer (41-43) measured the absorption of aqueous solutions containing up to 98.6% of nitric acid by weight, and found no maxima for concentrations greater than 63% (14 *N*): his data indicate that 92% acid (22 *N*) exhibits a higher intensity near 2600 Å than 99% acid (23.7 *N*) (*vide infra*). The absorption of 0.2 *N* potassium nitrate dissolved in sulphuric acid of increasing concentration was similar to that of increasing concentrations of nitric acid in water. Von Halban and Eisenbrand (19) investigated the absorption of nitric acid at concentrations up to 68% (15.3 *N*) and noted the decrease in the intensity of the nitrate ion band with increasing concentration. They also observed a maximum at 2650 Å in the spectrum of solutions of nitric acid in anhydrous ether and attributed this band to the presence of unionized HO-NO₂ molecules. Hantzsch (21, 22) found no maximum in the absorption curve of 100% nitric acid, nor in the curve of a solution of nitric acid in anhydrous ether; he did note that a band appeared on addition of a trace of water to such an ethereal solution. Hantzsch discusses both his own work and that of Von Halban and Eisenbrand in a long critical paper (22) in which he explains the effects of dilution on the spectrum of nitric acid in terms of a complex series of equilibria involving a hydrolysis of "nitracidium nitrate" {[ON(OH)₂]⁺ NO₃⁻}

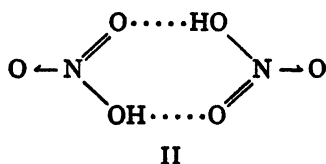
to a "pseudoacid" ($\text{O}_2\text{N}-\text{OH}$) followed by hydration of the pseudo acid and, on further addition of water, its conversion to "hydroxonium nitrate" $[(\text{NO}_2)\text{H}_3\text{O}]$ which then ionizes.

Although, as will be apparent later, the changes which occur on the increasing addition of water to anhydrous nitric acid must involve a series of equilibria comparable in complexity with those postulated by Hantzsch, most of this earlier spectrometric work would seem to be reconcilable with a simple ionic equilibrium between unionized nitric acid molecules ($\text{HO}-\text{NO}_2$) with an absorption maximum at 2600 to 2650 Å and a nitrate ion with a weaker absorption maximum at 3015 to 3020 Å, viz.,



Except for some measurements by Dalmon and Bellin (11, 12) and by Kortüm (33), little work appears to have been done recently on the ultraviolet absorption of concentrated solutions of nitric acid, but it is relevant to consider some measurements on other physical properties. The *refractive indices* of aqueous solutions of nitric acid when plotted against the per cent composition give a linear relation over the range from 78 to 91%. At 91% a sharp inflection occurs, and above 98.5% the slope of the line is reversed (48). The *electrical conductivity* also behaves abnormally over this concentration range, as was observed by Velej and Manley (48) and confirmed recently in these laboratories by Taylor (31).

Several investigators have examined the *infrared* and *Raman spectra* of aqueous solutions of nitric acid. Dalmon and Freyman (13) have recorded the very near infrared spectrum of 80 to 100% nitric acid, and have noted an absorption band at 1.017μ in the spectrum of the anhydrous acid, which they attributed to the associated molecule II. On the progressive addition of water this band diminishes in intensity and a new band develops at 0.97μ .



At a concentration of 80% the 1.017μ band has almost disappeared. Dalmon and Freyman consider that the 0.97μ band may be due to a hydroxyl group. These observations confirm earlier work of Kinsey and Ellis (32). A theoretical treatment of the infrared absorption spectrum of nitric acid has recently been attempted by Bauer and Magat (2), the results of which are claimed to be in accordance with the observations of Dalmon and Freyman.

Nitric acid below 30% gives a *Raman spectrum* similar to that of the alkali nitrates and differing from the spectrum of the concentrated acid (3, 7-9, 15, 35, 36, 38-40, 45).

When the concentration is increased above 30% new Raman lines appear. In the spectrum of the anhydrous acid no lines attributable to the nitrate ion

are observed; two faint lines ($\Delta \nu$ 1050 cm^{-1} and 1400 cm^{-1}) in the spectrum of anhydrous nitric acid were attributed by Chédin to nitrogen pentoxide, which he estimates may be present in anhydrous nitric acid to the extent of about 1%. Chédin observed that these weak bands can still be seen in acid of 99.6% concentration. Most of the studies on the Raman spectrum of nitric acid have been qualitative only, and no systematic studies over the range from 80 to 100% at small increments in concentration appear to have been made. This subject has been reviewed by Hibben (28).

Recently Bennett, Brand, and Williams (4, 5) have put forward evidence indicating that solutions of nitric acid in sulphuric acid may contain molecular species other than HONO_2 and NO_3^- , and they attribute the Raman line at 1400 cm^{-1} to the nitronium (NO_2^+) ion.

These abnormalities in the physical constants of concentrated nitric acid solutions are of particular interest in relation to the marked influence of acid concentration on the yields of RDX obtained in the nitration of hexamine. They suggest that some species of molecule or ion may be present in maximal concentration in nitric acid containing a small but significant amount of water, a molecule or ion which may be the primary agent in the nitration process.

Experimental Observations

The ultraviolet absorption spectra of aqueous solutions of nitric acid have been determined over the concentration range from 80 to 100% nitric acid. A maximum occurs at 2565 Å in the spectrum of the anhydrous acid with $E_{m_{\max}}$ 11.1. The position of the maximum shifts to 2615 Å as the concentration falls to 95% and remains unchanged with further dilution to 90%. With diminishing concentration the molecular extinction coefficient at the maximum decreases to 9.5 for 95% acid, increases again to 11.5 for an acid of 92% strength, and then falls slowly on further dilution. These changes are shown in the series of curves in Fig. 2. In Fig. 3 the value of $E_{m_{\max}}$ is plotted against the acid concentration. In Table III the wave lengths and the intensities at the maxima are listed for all the nitric acid samples studied. The value of $E_{m_{\max}}$ in the last column is an averaged value of two or more spectrographic measurements on the same acid sample. The reproducibility of $E_{m_{\max}}$ on a series of determinations on the same sample of diluted acid was about 2%. However, the values obtained for $E_{m_{\max}}$ on different preparations of acid diluted to approximately the same concentration varied in some cases by several per cent. These variations are responsible for the scatter of the points in Fig. 3. They are caused most probably by uncertainties in the determination of the acid concentration (see Experimental Section, page 602).

C. Nitric Acid – Ammonium Nitrate

It does not seem that the ultraviolet absorption spectrum of ammonium nitrate dissolved in anhydrous nitric acid has been determined previously, but Médard and Petitpas (35, 36) have examined the Raman spectra of such

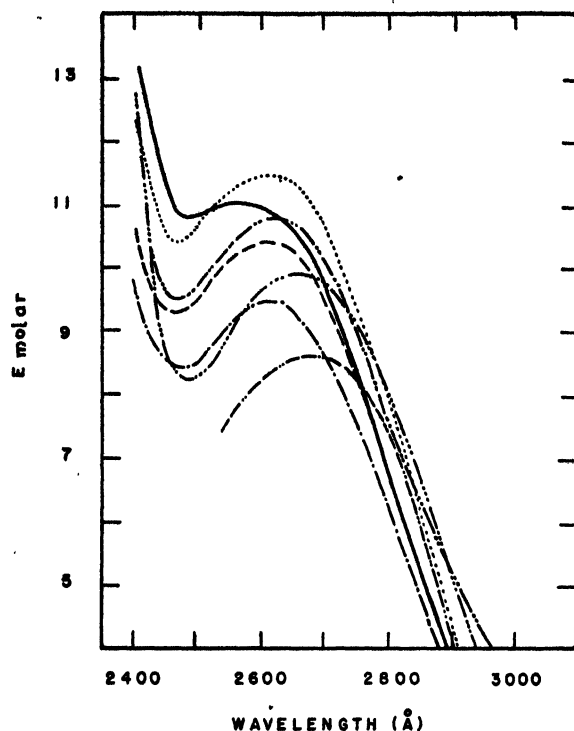


FIG. 2. Ultraviolet absorption spectra of aqueous nitric acid:—

—————	100.0% HNO_3	-----	90.0% HNO_3
-----	97.0%	80.1%
-----	95.0%	-----	68.6%*
.....	92.2%		

(*) Taken from data of von Halban and Eisenbrand (reference 19).

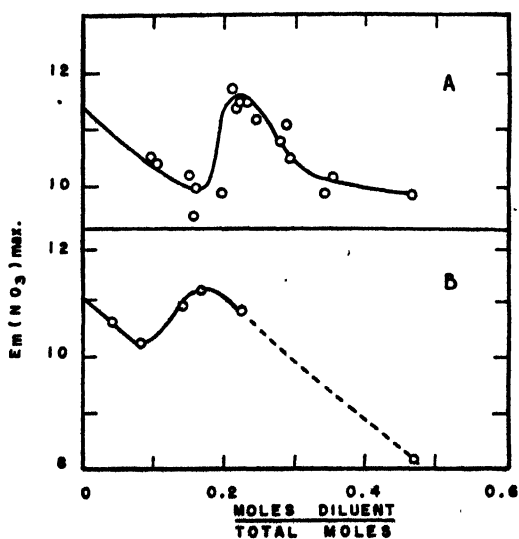


FIG. 3. Variation of the molecular extinction coefficient at the maximum for nitric acid.
A. Dilution with water; B. Dilution with ammonium nitrate.

TABLE III
ABSORPTION SPECTRUM OF 80 TO 100% NITRIC ACID. POSITION
AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	E_{max} (individual measurements on the same acid sample)	E_{max} (average)
% Nitric acid	Mole fraction of water			
100.0	0.000	2565	11.15, 11.30 11.10, 11.01 10.90	11.1
97.2	0.092	2600	10.40, 10.40, 10.80	10.5
96.9	0.101	2610	10.70, 10.55, 10.15	10.4
95.3	0.147	2610	10.40, 10.52, 9.90, 10.20	10.2
95.0	0.155	2610	9.54, 9.54	9.5
94.9	0.158	2610	9.92, 10.02	10.0
93.6	0.193	2615	9.84, 9.93	9.9
93.0	0.208	2610	11.68, 11.80	11.7
92.7	0.213	2615	11.43, 11.43	11.4
92.6	0.218	2610	11.80, 11.40, 11.40	11.5
92.2	0.228	2610	11.50, 11.48	11.5
91.7	0.240	2615	11.20	11.2
90.1	0.277	2615	10.80, 10.82	10.8
89.9	0.282	2615	11.10, 11.10	11.1
89.5	0.291	2625	10.60, 10.35	10.5
87.2	0.339	2635	9.90, 9.95	9.9
83.4	0.409	2650	10.30, 10.30, 10.15	10.2
80.1	0.465	2650	9.88, 10.00	9.9

solutions. They note that, on the addition of the salt, shifts occur in the positions of the Raman lines similar to those produced by the addition of small amounts of water.

Experimental Observations

The ultraviolet absorption spectra have been measured of solutions containing up to 54 gm. of ammonium nitrate in 100 gm. of solution.* The results are recorded in Table IV and in Fig. 4.

The effect of addition of ammonium nitrate on the ultraviolet absorption spectrum of anhydrous nitric acid parallels the effects noted by Médard on the Raman spectrum. Small additions cause a fall in the intensity of the absorption maximum near 2625 Å. Further addition of ammonium nitrate causes the intensity of E_{max} to increase and at higher concentrations it again falls. These variations are plotted against the concentration in Fig. 3. The considerable shift of the wave length of the absorption maximum in the mixture containing 54% ammonium nitrate is probably caused in part by the additive effect of the nitrate ion absorption maximum at 3015 Å contributed by the anion of the added salt.

* At the temperature at which these spectra were measured (approximately 20° C.) a two phase system occurs for nitric acid - ammonium nitrate mixtures over the concentration range between 27 and 52% of ammonium nitrate by weight. A single phase is obtained between 52 and 57% and below 27% ammonium nitrate.

TABLE IV

ABSORPTION SPECTRUM OF NITRIC ACID - AMMONIUM NITRATE. POSITION AND INTENSITY OF THE MAXIMUM

Concentration		Wave length of maximum, Å	$E_{max} (NO_2)^*$
% NH_4NO_3	Mole fraction NH_4NO_3		
0.0	0.000	2565	11.1
5.0	0.040	2615	10.6
10.0	0.080	2625	10.3
17.0	0.139	2635	10.9
20.0	0.165	2650	11.2
26.8	0.224	2665	10.8
54.0	0.470	2775	8.2

* See page 598.

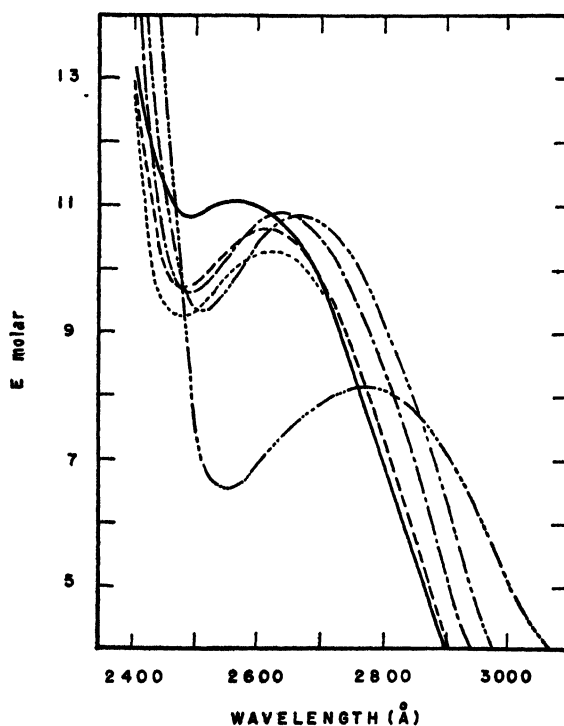


FIG. 4. Ultraviolet absorption spectra of nitric acid - ammonium nitrate mixtures.

—————	100.0% HNO_3	-----	17.0% NH_4NO_3
-----	5.0% NH_4NO_3	-----	26.8% "
.....	10.0% "	-----	54.0% "

D. Nitric Acid - Potassium Nitrate

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 25% of potassium nitrate in anhydrous nitric acid are shown in Fig. 5, and the

variation of E_{max} is plotted in terms of the mole fraction of potassium nitrate in Curve A of Fig. 8.

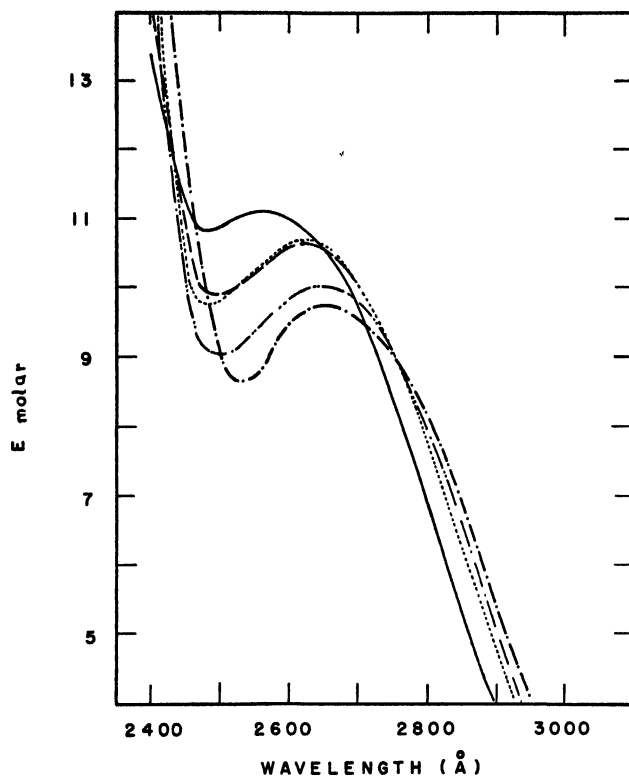


FIG. 5. Ultraviolet absorption spectra of nitric acid - potassium nitrate mixtures.

—————	100.0% HNO ₃	- - - - -	20.0% KNO ₃
- - - - -	10.0% KNO ₃	— · — · —	25.0% KNO ₃
·········	15.0% KNO ₃		

There is a suggestion that E_{max} does not diminish steadily, and an inflexion may be present in the neighborhood of 0.1 mole potassium nitrate. A similarity to the behavior of the nitric acid-ammonium nitrate system is indicated but the data are insufficient to establish this with certainty.

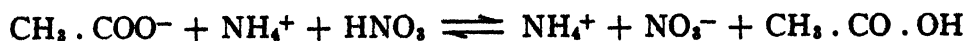
E. Nitric Acid - Ammonium Acetate

Experimental Observations

The spectra of solutions containing up to 30% of ammonium acetate in anhydrous nitric acid are recorded in Fig. 6. As with the other binary systems of salts with nitric acid, there is a suggestion of a fall and subsequent rise to a maximum in the curve of E_{max} plotted against increasing concentration of the added salt (Fig. 8).

During the manipulation of these solutions the odor of acetic acid seemed to increase as the concentration of the ammonium acetate became larger.

In order to determine whether acetic acid was being produced in accordance with the equilibrium:



a ternary solution of ammonium nitrate, nitric acid, and glacial acetic acid was prepared; the molecular proportions of the three constituents were

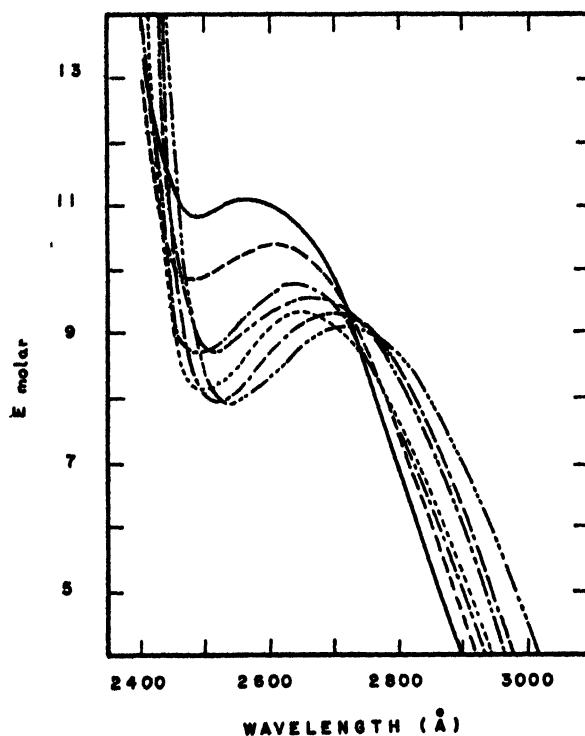


FIG. 6. Ultraviolet absorption spectra of nitric acid - ammonium acetate mixtures.

—————	100.0% HNO_3	- - - - -	20.6% NH_4OAc .
- - - - -	5.0% NH_4OAc .	- - - - -	25.0% "
- · - · - ·	9.8% "	- · - · - ·	29.9% "
·····	15.0% "		

adjusted to yield the same molar proportions* as in the most concentrated of the ammonium acetate - nitric acid solutions shown in Fig. 6. Both the densities and the absorption spectra of these two solutions were the same. Taylor (46) has investigated the electrical conductivity of mixtures of nitric acid, acetic acid, and ammonium acetate, and has observed that solutions of identical conductivity can be prepared by mixing either ammonium acetate and nitric acid or ammonium nitrate and acetic acid in suitable proportions.

*For the curve indicated as —····—···· the mole fraction of ammonium acetate was 0.259. This ternary solution was made up to have a mole fraction of acetic acid of 0.258, ammonium nitrate 0.258, and nitric acid 0.484. The molecular extinction coefficient at the maximum calculated for nitric acid was 9.0, and can be compared with 9.1 for the ammonium acetate - nitric acid solution.

F. Nitric Acid - Acetic Acid

Viscosity and freezing point measurements suggest that compound formation may occur between these two acids, but the Raman spectra of such mixtures exhibit the characteristic frequencies of each component without the appearance of any new lines (6).

Experimental Observations

The ultraviolet absorption spectra of solutions containing up to 50% of anhydrous acetic acid in anhydrous nitric acid are shown in Fig. 7. When

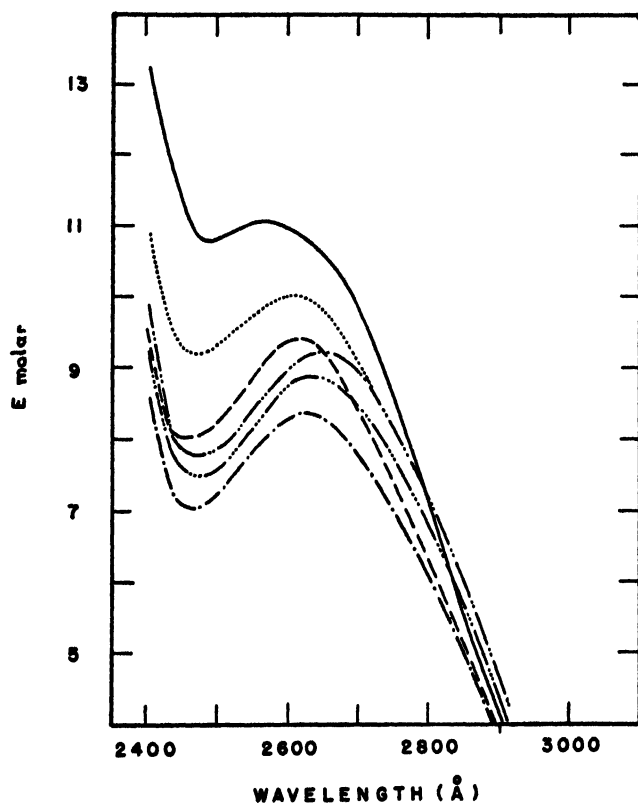


FIG. 7. Ultraviolet absorption spectra of nitric acid - acetic acid mixtures.

—————	100.0% HNO ₃	- - - - -	30.6% HOAc.
.....	7.0% HOAc.	- · - · -	39.0% "
- - - - -	12.3% "	- · - · -	49.4% "

the intensity at the maximum is plotted against the composition of the solution, the same type of curve is obtained as with the other binary systems containing nitric acid (Fig. 8).

G, H, I. Nitrogen Pentoxide

The changes in the absorption spectrum of anhydrous nitric acid brought about by the addition of small quantities of water or other solutes might arise

from the effects of the solute on an equilibrium, in "anhydrous nitric acid," between nitric acid, water, and nitrogen pentoxide, viz.:—



This consideration prompted the extension of these investigations to include systems containing nitrogen pentoxide.

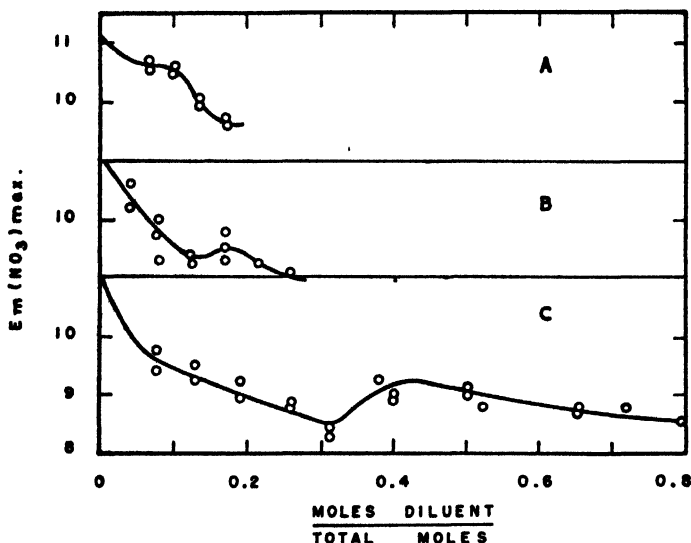


FIG. 8. Variation of the molecular extinction coefficient at the maximum for nitric acid.

- A. Dilution with potassium nitrate.
- B. Dilution with ammonium acetate.
- C. Dilution with acetic acid.

Experimental Observations

The spectra of nitrogen pentoxide in acetic acid, acetic anhydride, and in carbon tetrachloride are recorded in Fig. 9. These show no maxima, but indicate that the absorption is very intense below 2700 Å. In acetic acid the spectrum differs somewhat from that in the other solvents, there being evidence of an inflection at 2750 Å.

J. Nitric Acid – Nitrogen Pentoxide

Experimental Observations

The spectra of solutions of anhydrous nitric acid containing up to 24% by weight of nitrogen pentoxide are recorded in Fig. 10. It is seen that as the amount of nitrogen pentoxide is increased, the absorption maximum at 2615 Å soon becomes obliterated by the intense absorption of the added solute.

K. Nitric Acid – Acetic Anhydride

Experimental Observations

The range of concentration over which this system can be investigated is limited, since, at room temperature, mixtures containing from 12 to 94% of

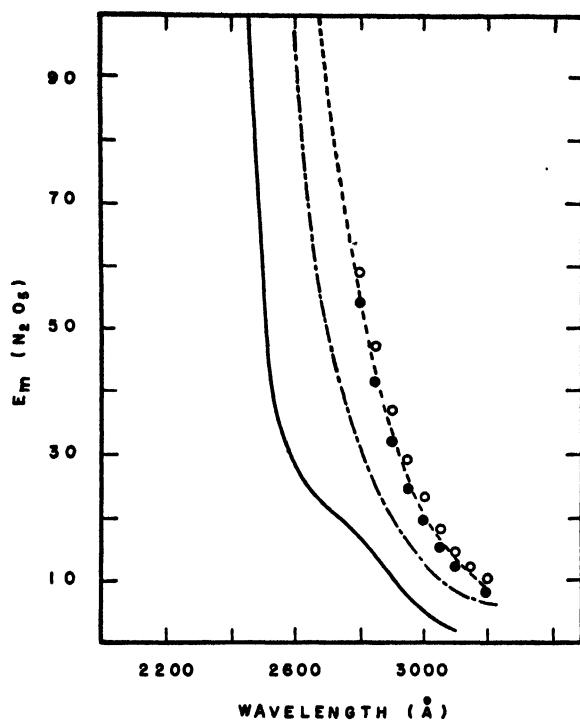


FIG. 9. Ultraviolet absorption spectrum of nitrogen pentoxide in various solvents.

————— 0.054 molar solution in acetic acid.
 - · - · - · - 4.79 molar solution in acetic anhydride.
 ———●●●—— 0.282 molar solution in carbon tetrachloride.
 ———○ ○ ○—— 0.102 molar solution in carbon tetrachloride.

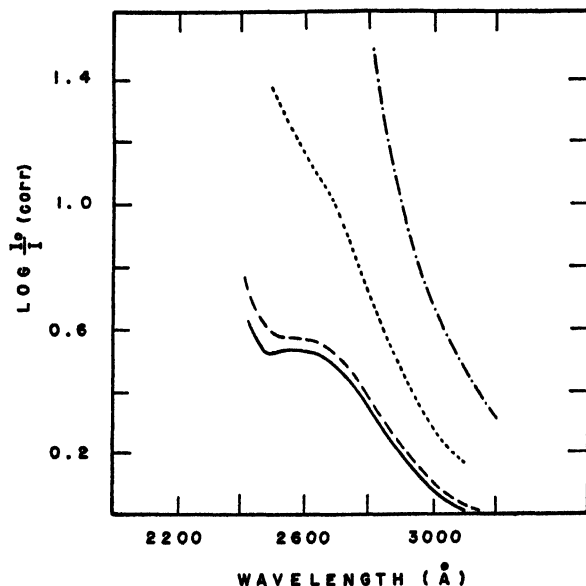


FIG. 10. Ultraviolet absorption spectra of nitric acid-nitrogen pentoxide mixtures (optical density corrected for change in the specific gravity of the solution. See page 598).

————— 100% HNO_3
 - - - - - 3% N_2O_5
 - · - · - · - 12% N_2O_5
 - · - · - · - 24% N_2O_5
 (Cell thickness 0.0196 mm.)

acetic anhydride are unstable and are liable to undergo spontaneous decomposition. The spectra of mixtures outside of this unstable range which were examined are shown in Fig. 11. These curves exhibit significant similarities

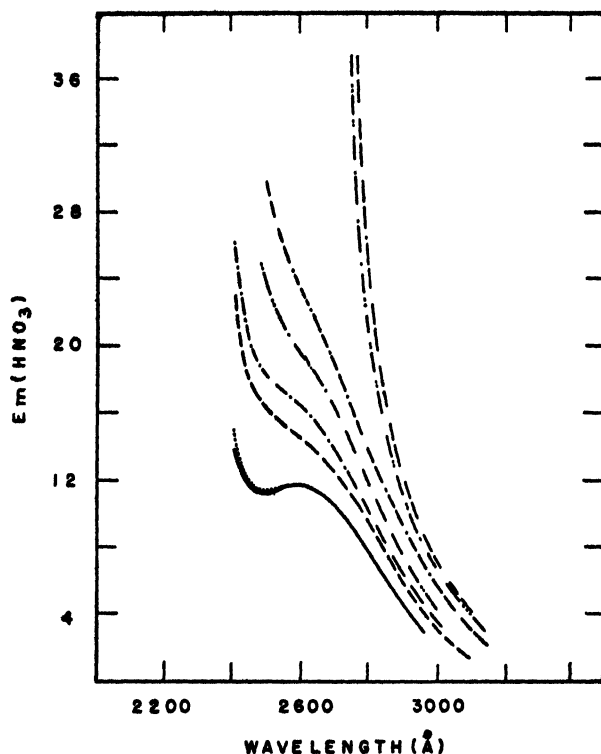


FIG. 11. Ultraviolet absorption spectra of nitric acid - acetic anhydride mixtures.

—————	1.26% Ac_2O	-----	12.16% Ac_2O
.....	3.19% "	94.72% "
- - - - -	6.74% "	96.84% "
.....	7.24% "		
.....	9.46% "		

to the curves for the nitric acid - nitrogen pentoxide system shown in Fig. 10. At high concentrations of acetic anhydride the curves resemble those of high concentrations of nitrogen pentoxide in nitric acid, and at low concentrations of acetic anhydride they resemble the solutions of low concentrations of nitrogen pentoxide in nitric acid. Since acetic anhydride is nonabsorbent in this region of the spectrum (24, 34), these observations suggest the existence of an equilibrium:—



in which the equilibrium position lies well to the right-hand side.

Discussion

A comparison of the absorption spectra of nitric acid solutions containing small amounts of water (Fig. 2) with the spectra of nitric acid solutions

containing small amounts of nitrogen pentoxide (Fig. 10) suggests that the latter group of curves manifest a continuation of a series of changes which commences with the 95% acid and passes smoothly through the anhydrous acid to the acids containing excess nitrogen pentoxide.*

With this in mind, the changes in the spectra of aqueous nitric acid which occur over the concentration range from 80 to 100% may be described in the following terms. Between 80 and 95% a molecular species predominates which is responsible for the absorption maximum near 2600 Å. This molecule or ion, which may be designated the "2600 Å chromogen" is present in maximal concentration at 91 to 92%. At 95 to 96%, changes occur in the spectrum which can be attributed to the presence of "free nitrogen pentoxide" in the solution.

In Table V the *persistence* of the 2600 Å band is listed for various concentrations; the persistence is defined as the ratio of the molecular extinction coefficient at the maximum near 2600 Å to that at the minimum near 2500 Å. The persistence constitutes a convenient numerical index of the prominence of the absorption band, and its continuous diminution with increasing nitric acid concentration indicates that the curve is progressively flattening. This effect is superimposed on the rise of E_{2600} to a maximum at 91 to 92%.

It would seem necessary to invoke two variables to explain these changes, (a) an increase in the concentration of the 2600 Å chromogen between 80 and 92% and (b) the appearance of a new molecular or ionic species exhibiting intense structureless absorption, which we have tentatively identified above as "free nitrogen pentoxide."

Examination of the persistence values in Table V shows furthermore that between 97 and 100% the rate of fall is greater than at lower nitric acid concentrations, indicating that small decreases in water content produce progressively greater increases in the "free nitrogen pentoxide" concentration as the anhydrous condition is approached.†

Between 93 and 96% the absolute intensity of the maximum falls off. In view of the very great intensity of the nitrogen pentoxide absorption, the concentrations of this substance required to produce the observed flattening

* Hantzsch (22) has questioned the claim of von Halban and Eisenbrand (19) that an ethereal solution of anhydrous nitric acid possesses an absorption maximum at 2650 Å; he reported that no such maximum is present if the ether is truly anhydrous, a maximum appearing only on the addition of a drop of water to the solution. Hantzsch also failed to observe any maximum in the absorption spectrum of anhydrous nitric acid. One would infer from Hantzsch's paper that the maximum observed by von Halban and Eisenbrand resulted from the use of moist ether. Hantzsch's failure to detect the maximum in the spectrum of nitric acid, either in the free state or in ethereal solution, might very well be caused by his using anhydrous nitric acid containing appreciable quantities of dissolved nitrogen pentoxide.

† One of the referees has commented on our use of the persistence concept and has suggested that we try to use the E values to calculate the percentage of nitrogen pentoxide present at various concentrations. This had been considered previously, but the idea was discarded since the molecule or ion actually contributing to the absorption which we attribute to "free nitrogen pentoxide" is almost certainly a constituent of an equilibrium mixture and its absorption is very unlikely to obey a Beer's law relation based on the nitrogen pentoxide curves in Fig. 9. A strict mathematical treatment of the curves seemed of doubtful significance in these circumstances. We therefore used the persistence treatment so as to be able to describe the changes of curve shape with concentration in a semiquantitative manner.

TABLE V
PERSISTENCE OF THE 2600 Å BAND IN NITRIC ACID - WATER

% HNO ₃	E_{\max}/E_{\min}	% HNO ₃	E_{\max}/E_{\min}
100	1.02	90	1.14
97	1.12	87	1.17
95	1.13	80	1.20

effect must be exceedingly small, and it would seem reasonable to surmise that in addition to the formation of free nitrogen pentoxide, other factors may be operative over this concentration range in reducing the concentration of the 2600 chromogen.

The nature of the 2600 chromogen has been discussed by earlier workers, and von Halban and Eisenbrand (19) identify it with the nonassociated HO-NO₂ molecule (Hantzsch's pseudoacid). This would seem to be largely a speculative hypothesis, although it is supported to some extent by the resemblance to the spectrum of the alkyl nitrate esters (Fig. 1). The effect of the addition of small amounts of water, acetic acid, or various inorganic salts in bringing about an increase in the concentration of this species is difficult to explain. If the existence of associated molecules which are non-absorbent in this region of the spectrum be postulated, the observed effects could be explained by assuming that the added solute brings about a "deassociation". This would be in line with Dalmon and Freyman's interpretation of the changes in the infrared spectrum of nitric acid on dilution with water to 80% (see page 584).

It is relevant to note here that the system nitric acid - ammonium nitrate exhibits no unusual features over the measured concentration range which would suggest specific complex formation or other abnormal type of behavior to account for its essential role in the Bachman process for the manufacture of RDX.

Nitrogen Pentoxide

The main source of information concerning the presence of nitrogen pentoxide in nitric acid is the Raman spectrum (28). It has already been noted (page 584) that in the Raman spectrum of anhydrous nitric acid a line appears at $\Delta\nu = 1400\text{ cm}^{-1}$. This line is very prominent in anhydrous nitric acid containing 20% of phosphorus pentoxide, as also are two lines 1050 and 1100 cm^{-1} , which are faint in the spectrum of pure anhydrous nitric acid. In the Raman spectrum of crystalline nitrogen pentoxide there are two lines at 1050 and 1400 cm^{-1} which are identical in position with those which augment in intensity on addition of nitrogen pentoxide to anhydrous nitric acid. The same lines occur also in the Raman spectra of certain nitric acid - sulphuric acid mixtures (4, 5, 9).

These lines are not seen in the spectra of solutions of nitrogen pentoxide in carbon tetrachloride or phosphorus oxychloride, there being instead three other prominent lines near 1330, 1250, and 880 cm^{-1} . The infrared spectrum of gaseous nitrogen pentoxide is very similar to that of a solution in carbon tetrachloride (10, 27). The evidence from Raman and infrared spectra thus indicates that nitrogen pentoxide exists in one form in the gaseous state and in solution in chlorinated solvents, and in a different form in the crystalline state and in solution in anhydrous nitric acid.

Bennett, Brand, and Williams (4, 5) have drawn attention to these anomalies in the Raman spectrum of anhydrous nitric acid, and in support of their contention that the Raman line at 1400 cm^{-1} in mixtures of nitric acid – sulphuric acid is caused by the NO_2^+ ion they make use of the ingenious argument that such an ion would be isosteric with carbon dioxide and might be expected to possess similar vibrational characteristics. Carbon dioxide possesses a prominent Raman line near 1400 cm^{-1} . It would seem to us that this hypothesis necessitates the further conclusion that, as a line is present also at the same frequency in the Raman spectrum of nitrogen pentoxide in the crystalline state, that too contains the NO_2^+ ion, suggesting an ionic lattice structure of NO_2^+ and NO_3^- ions. If this is so, some evidence of the presence of NO_3^- might be expected to show up in the infrared spectrum of crystalline nitrogen pentoxide.*

Up to 1946 no real evidence of the presence of NO_2^+ or other nitrogen containing cation in nitric acid (in the absence of sulphuric acid) had been obtained, except possibly for Hantzsch and Berger's observation (23) that, on the electrolysis of "nitracidium perchlorate" in nitromethane solution there occurs a migration of nitrogen containing groups toward the cathode. In these laboratories Taylor, Lyne, and Follows have investigated the electrical conductivity of the system water – nitric acid – nitrogen pentoxide and shown that the equivalent conductivity is minimal for 96% acid, increases sharply as the acid approaches the anhydrous condition, and continues to increase smoothly as nitrogen pentoxide is added. This would indicate an increase in the ionic population of the solution above 96%. To explain this, Taylor suggested that nitrogen pentoxide may be undergoing ionic dissociation as shown below; such dissociation need not be extensive to explain the observed conductivity changes.



The ultraviolet absorption spectra of the water – nitric acid – nitrogen pentoxide system are readily reconcilable with this hypothesis. In such a system the weak absorption of the nitrate ion at 3020 Å may be obliterated by more intense "nitrogen pentoxide absorption". The latter might be caused by the NO_2^+ ion, or by the undissociated nitrogen pentoxide molecule.

* A similar hypothesis concerning the structure of crystalline nitrogen pentoxide has been advanced by Ingold, Millen, and Poole (30).

coefficients from these measurements it was necessary to know the molar concentration, which involved the determination of the specific gravities of the solutions. Such measurements of specific gravity have been carried out on the following systems:—

Nitric acid – ammonium nitrate

Nitric acid – potassium nitrate

Nitric acid – ammonium acetate

Nitric acid – acetic acid.

The results are given in Table VI and in Fig. 12.

TABLE VI
DENSITIES OF ANHYDROUS NITRIC ACID SOLUTIONS

% NH_4NO_3	D_4^{20}	% KNO_3	D_4^{20}	% NH_4OAc	D_4^{20}	% HOAc	D_4^{20}	% N_2O_5	D_4^{25} *
0.00	1.513	—	—	—	—	—	—	0.0	1.501
5.01	1.527	9.98	1.582	5.02	1.508	12.70	1.441	6.0	1.530
10.81	1.548	14.97	1.621	9.84	1.501	28.40	1.361	12.0	1.560
19.72	1.568	19.99	1.658	14.95	1.491	37.17	1.322	18.0	1.588
26.75	1.579	25.00	1.695	20.60	1.478	49.40	1.265	24.0	1.618
54.00	1.578	—	—	25.00	1.459	66.37	1.186	30.0	1.645
—	—	—	—	29.90	1.440	79.70	1.131	—	—

* Data supplied by Dr. E. G. Taylor

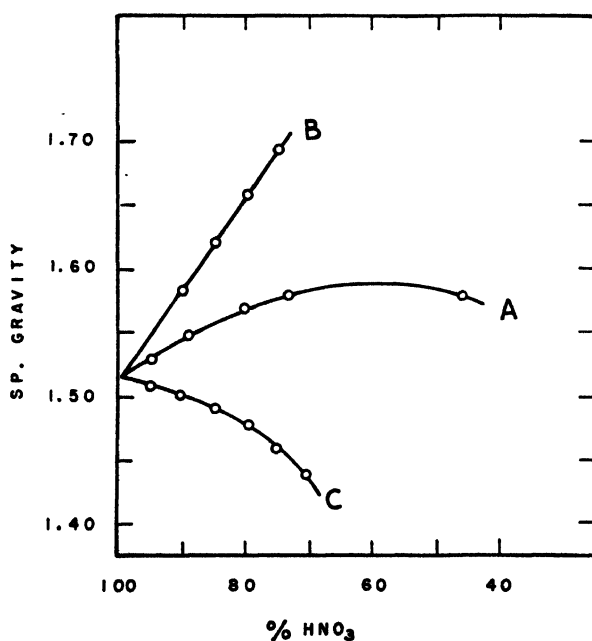


FIG. 12. Specific gravities (d_4^{20}).

A. Nitric acid – ammonium nitrate.

B. Nitric acid – potassium nitrate.

C. Nitric acid – ammonium acetate.

The values for the specific gravity of aqueous solutions of nitric acid were taken from the International Critical Tables, and for solutions of nitrogen pentoxide in nitric acid from measurements made by Dr. Taylor in this laboratory. Approximate values for nitrogen pentoxide in acetic anhydride and in carbon tetrachloride were obtained by interpolation between the specific gravity values of solid nitrogen pentoxide (2.0), acetic anhydride (1.08), and carbon tetrachloride (1.59), assuming a linear variation with concentration. The data in Table VI represent the mean of duplicate determinations based on comparison of the weight of 10 ml. of solution with 10 ml. of water, using a volumetric flask as a pyknometer. Measurements were made at $20.0 \pm 0.1^\circ \text{C.}$, and a correction for buoyancy applied. The precision in most cases is better than 0.001, and in no case was a variation greater than 0.002 observed.

Spectrographic Manipulation

A Beckman model DU ultraviolet spectrophotometer was used for the determination of the spectra. The majority of the solutions possessed too great an optical density to permit use of the standard 1 cm. cells. Cells were designed as shown in Fig. 13. They consisted of optically plane quartz disks

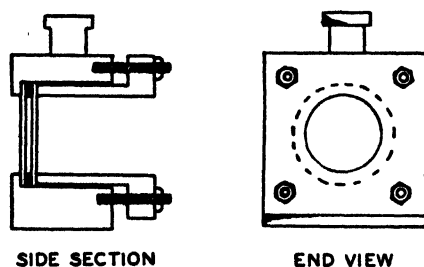


FIG. 13. Thin cell for corrosive solutions.

separated by platinum annuli and held in place in an aluminum holder. The quartz disks were 1 mm. thick and 26 mm. in diameter. The annuli were stamped from platinum sheet of 0.012, 0.1, and 1 mm. thickness. Aluminum and platinum were used as the metals most suitable to withstand the action of concentrated nitric acid (47).

A specially designed compartment containing a sliding carriage to hold two of these cells was placed between the main case of the spectrograph and the photocell compartment. Two quartz windows permitted entrance and exit of the monochromatic light beam through this compartment, and provision was made for the aspiration of a stream of air through the compartment to remove any corrosive fumes from the neighborhood of the spectrophotometer.

The cells were calibrated photometrically using potassium chromate (20, 29). The potassium chromate was recrystallized four times from 0.005 *N* potassium hydroxide and dried by pumping at 10^{-5} mm. for five hours. Several determinations of the optical density of standard chromate solutions

were made for each cell. Using the value of E_{\max} given by Hogness *et al.* (29) the cell thickness (l) was calculated from Equation (1).*

Two methods were employed in filling these cells. In the first method, which could be employed only for nonhygroscopic and nonvolatile material, the annulus and one quartz disk were placed on the inner section of the aluminum holder. A few drops of the liquid were then placed on the quartz disk. The second quartz disk was then lowered on to the annulus, after which the outer section of the holder was slipped over the inner section and tightened (Fig. 14a).

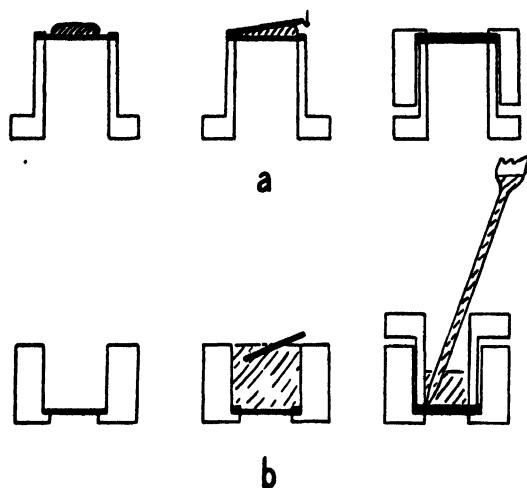


FIG. 14. Diagrammatic illustration of technique for filling thin cell.

- a. For nonhygroscopic solutions.
- b. For hygroscopic solutions.

The second method was used for hygroscopic acids. The outer section of the aluminum holder was placed in a shallow crystallizing dish, and one quartz disk lowered into place. The cavity of the cell holder was filled with the acid solution and the annulus and second quartz disk then slid into the solution and pushed down into place with a glass rod. The inner section of the holder was inserted, the excess acid removed with a pipette, and the whole tightened. Using this method of filling, the portion of solution which is confined between the quartz disks is never exposed to the air in a thin film (see Fig. 14b).

Reagents and Materials

Ammonium nitrate and ammonium acetate—Merck Reagent grade.

Potassium nitrate—"Analar" Reagent.

The ammonium nitrate and potassium nitrate were found to contain less than 0.1% moisture and were therefore used without further treatment.

* In these calculations it is assumed that Beer's law holds accurately for solutions of potassium chromate over the concentrations used. The validity of this assumption is demonstrated by the agreement in the values of the molecular extinction coefficients for ammonium nitrate solutions (Table II) obtained with the same solution in cells of different thickness, since these cell thicknesses are based on measurements of the potassium chromate solutions as described above.

The ammonium acetate was pumped at 1 mm. pressure for several hours and used directly after pumping.

The nitric acid was prepared in an all-glass still. A mixture of two parts by volume of 96% sulphuric acid and one part of 70% nitric acid was distilled at a pressure of 30 mm. of mercury at 60° to 70°. A water-white product was obtained of 99.5 to 100.5% nitric acid content, which gave no test for chloride or sulphate ion. Solutions of lower concentration were prepared by diluting 40 or 50 gm. of the anhydrous acid with the calculated weight of water. The final concentration was determined by titrating a diluted sample with 0.2 *N* sodium hydroxide using phenolphthalein as indicator.

The acetic acid, acetic anhydride, and nitric acid – nitrogen pentoxide mixtures were prepared by Dr. E. G. Taylor and Dr. A. G. Follows in connection with investigations of electric conductivity carried out simultaneously with these spectrographic measurements. The acetic acid was obtained by careful fractionation of Reagent grade glacial acetic acid, the purity being checked by freezing point determinations. The acetic anhydride was distilled from calcium carbide and then fractionally redistilled. Nitrogen pentoxide was prepared by distillation of equal parts by weight of phosphorus pentoxide and anhydrous nitric acid at reduced pressure.

Acknowledgments

During the course of these investigations we had many fruitful discussions with Dr. E. G. Taylor, whose studies of the electrical conductivities and phase diagrams of certain of these systems will be published separately. Our thanks are also due to Dr. A. G. Follows and Mr. M. Lyne for supplies of anhydrous nitric acid and nitrogen pentoxide.

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THE SEPARATION OF ISOLINOLEIC ACID FROM HYDROGENATED LINSEED OIL BY CHROMATOGRAPHIC METHODS¹

BY H. W. LEMON

Abstract

When linseed oil or other oils containing linolenic acid are hydrogenated, an isomeric linoleic acid (isolinoic acid) is formed. Its concentration increases to a maximum, then decreases as hydrogenation proceeds. In view of the possible relationship of this acid to "flavor reversion", its separation in pure form has been investigated. Concentrates of isolinoic acid or its methyl ester were obtained from partially hydrogenated linseed oil by crystallizing a large proportion of the more saturated acids or methyl esters from a solvent at low temperatures. Further fractionation of such concentrates by chromatographic methods was investigated. Silica gel was found to be better for the purpose than either activated alumina or activated carbon. Methyl isolinoate was adsorbed more firmly on the silica gel than the less unsaturated esters, which were eluted by means of large volumes of hexane. Subsequent elution with chloroform removed the methyl isolinoate.

Introduction

When linseed oil or other oils containing linolenic acid are hydrogenated, an isomeric linoleic acid is formed in which the double bonds are in such positions that diene conjugation is not produced by high-temperature saponification (1, 15). In a typical hydrogenation of linseed oil, the concentration of isolinoic acid reached a maximum of 18% of the total fatty acids at an iodine value of approximately 100, then decreased on further hydrogenation.

Evidence has been presented that decomposition of isolinoic acid may give rise to the characteristic odor and flavor that develops in partially hydrogenated linseed oil, particularly on heating (15, 16). This deterioration is commonly called "flavor reversion".

In view of the possible relationship of isolinoic acid to flavor reversion, the separation of the acid in pure form by (a) fractional crystallization from a solvent at low temperature and (b) chromatographic methods has been investigated. The first method has been applied successfully by Brown *et al.* to the separation of a number of pure fatty acids (3, 4, 10, 11). The second method has been investigated by Cassidy (5, 6, 7), Kaufmann (13, 14), Graff and Skau (12), Dutton (9), Swift, Rose, and Jamieson (19), Riemenschneider, Herb, and Nichols (18), Claesson (8), and others. It was previously reported

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(15) that an isolinoleic acid concentrate of iodine value 152 was separated by the crystallization procedure of Brown *et al.*, but attempts to separate the pure acid by this method were not successful. Therefore further purification of the concentrates by chromatographic methods has been tried, and this work will be described in this paper.

Experimental

Linseed oil hydrogenated to an iodine value between 75 and 80, and containing no trace of linolenic acid, as indicated by the analytical method of Mitchell, Kraybill, and Zscheile (17), was saponified and the mixed fatty acids were separated. A 5% solution of the mixed acids in acetone was cooled to -20°C . while being agitated; this caused considerable crystallization. Filtration was achieved by suction, using a porous stone immersed in the mixture. The crystals were washed with a little acetone at -20°C ., the mixture filtered, and the filtrates combined. This solution was treated in the same manner, but at -50°C ., and the resulting filtrate was also treated in the same manner, but at -65°C . The filtrate was now concentrated to about one-quarter of its volume and again allowed to crystallize at -65°C . Acetone was removed from the final filtrate by distillation, and the resulting isolinoleic acid concentrate had an iodine value of 150 to 155. Attempts at further purification by crystallization were not successful. Some of the isolinoleic acid concentrate prepared in this way was converted to the methyl esters and distilled *in vacuo*.

A concentrate of methyl esters that proved to be a satisfactory starting material for chromatographic separations was obtained more simply, in the following manner. The hydrogenated linseed oil was converted to methyl esters by alcoholysis, using the method of Wright, *et al.* (20). A solution of 100 gm. of esters in 400 ml. of hexane was stored in a cabinet at -18°C . for 18 to 24 hr. The mass of crystalline esters was separated by filtration, the filtrate concentrated, chilled to -70°C ., and again filtered. Esters with an iodine value of about 120 were obtained.

Activated alumina, activated carbon, and silica gel were used as adsorbents. The alumina samples used were chromatographic grades with an activity equivalent to 1 or 2 on the Brockmann scale (2). Samples of activity 4 and 5 on this scale were prepared from these by exposure to moist air.

The activated carbon used was Darco G 60, manufactured by Darco Corporation, New York. It was mixed with an equal weight of Johns-Manville Hyflo Super-cel.

The silica gel was a commercial grade, 28–200 mesh, obtained from the Davison Chemical Corporation, Baltimore, Maryland.

The adsorbents were packed in glass columns and were flooded with the solvent to be used. The solution of fatty acids or esters was then added to the top of the column. Large volumes of solvent were allowed to pass through the adsorbent, the eluate was collected in fractions, the solvent was

removed by distillation, the residue weighed, and refractive index and iodine number determinations made when possible.

Results

(a) Activated Alumina

A number of experiments were tried using activated alumina of various activities, and various ratios of methyl esters to alumina. The solvent was petroleum ether. Methyl isolinoleate adhered most firmly to the alumina, and was difficult to remove. It is probable that a method could be developed with the use of this adsorbent, but, owing to the difficulties encountered, it was abandoned.

(b) Activated Carbon

Fractionation of both fatty acid and methyl ester concentrates by means of activated carbon was investigated. In both cases, a fraction with a higher iodine value than that of the original concentrate came through the column at the beginning of elution with petroleum ether, followed later by more saturated fractions. The results of one experiment using a concentrate of methyl esters are given in Table I. The process was very slow, and pure isolinoleic acid was not obtained by one passage of the acids or esters through the column.

TABLE I

SEPARATION OF METHYL ESTERS CONTAINING METHYL ISOLINOLEATE, BY ADSORPTION ON ACTIVATED CARBON

Contents of column:— 15 gm. Darco G. 60 } mixed
15 gm. Filter aid }
1 gm. of methyl esters, iodine value 141

Solvent:— Petroleum ether

Sample No.	Volume of eluate, cc.	Weight of esters, gm.	Iodine value of esters
1 to 2	125	0.02	
3 to 6	100	0.21	162
7 to 10	100	0.22	151
11 to 15	125	0.12	128
16 to 26	275	0.16	

NOTE:— Esters recovered 0.73 gm.

(c) Silica gel

Silica gel proved to be the most practical of the three adsorbents. When petroleum ether or hexane was used as solvent, methyl isolinoleate in a methyl ester concentrate was more firmly adsorbed than the more saturated esters, which were separated from the silica gel by elution with large volumes of the solvent. The adsorbed methyl isolinoleate was released by passing chloroform through the column, and the esters obtained had an iodine value close to the theoretical value of 172.3 for the pure ester. The ratio of esters to adsorbent was 1 to 10. The results of three experiments are given in Table II.

TABLE II

SEPARATION OF METHYL ISOLINOLEATE BY ADSORPTION ON SILICA GEL

Volume of eluate, cc.	Weight of esters eluted, gm.	Refractive index, 20° C.	Iodine value
<i>Experiment I. 20 gm. silica gel. 2.1 gm. methyl esters (iodine value, 144). Solvent: petroleum ether, followed by chloroform.</i>			
Petroleum ether			
700	0.016	1.4566	
500	0.119	1.4530	
500	0.118	1.4539	
500	0.179	1.4545	
500	0.178	1.4549	
500	0.166	1.4560	
500	0.159	1.4570	
1000	0.162	1.4601	
1200	0.143	1.4608	
Total 5900	1.240		
Chloroform			
100	0.703	1.4615	173
100	0.038	1.4650	
100	0.049	1.4670	
Total 300	0.790		
<i>Experiment II. 250 gm. silica gel. 25 gm. methyl esters (iodine value, 145). Solvent: petroleum ether, followed by chloroform</i>			
Petroleum ether			
65000	10.5	1.4546	103
Chloroform			
500	6.1	1.4606	167
500	3.4	1.4613	170
500	0.95	1.4616	174
500	0.46	1.4636	181
<i>Experiment III. 250 gm. silica gel. 25 gm. methyl esters (iodine value, 117). Solvent: hexane, followed by chloroform</i>			
Hexane			
73000	16.1	1.4551	96
Chloroform			
500	3.2	1.4598	168
500	1.8	1.4606	170
500	1.0	1.4608	172
1500	0.8	1.4633	173
1000	0.3	1.4648	173

The steadily rising refractive indices of the fractions separated from the adsorbent in Expt. I by elution with petroleum ether show that the most saturated esters came through the column first, followed by fractions of increasing unsaturation, undoubtedly containing some quantity of methyl isolinoleate. It is important that elution with hexane or petroleum ether be continued no longer than is necessary to remove the more saturated esters if a good yield of methyl isolinoleate is to be obtained.

On eluting the column with chloroform, fractions varying in iodine number between 167 and 180 have been obtained. As the theoretical iodine number for linoleic acid is 172.3, it is obvious that there was a small amount of a more unsaturated substance present. The refractive index of the best methyl isolinoleate samples was approximately 1.4613 at 20° C. When elution with chloroform was continued, more viscous fractions with higher refractive index values were obtained. These may have been polymers.

The linolenic and linoleic acid content of the methyl isolinoleate concentrate, of the purified methyl isolinoleate from the adsorption column, and of the esters eluted from the column with hexane have been estimated by the spectral method (17). The amounts of these acids present were so small that accurate values were not obtained. In each case linolenic acid was of the order of 0.1% and linoleic acid about 1.0% of the total fatty acids.

The ultraviolet absorption of a solution of the purified methyl isolinoleate in isoöctane has been determined. This revealed that it contained a small amount of a substance having triene conjugation. The extinction value ($E_{1\%}^{1\text{cm.}}$) at 268 $m\mu$ was 1.4.

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THE SIGNIFICANCE OF AN ABSORPTION BAND AT 968 CM.⁻¹ IN THE INFRARED SPECTRUM OF METHYL ISOLINOLEATE¹

BY H. W. LEMON AND C. K. CROSS

Abstract

The infrared absorption spectrum of methyl isolinoleate, separated from the methyl esters of hydrogenated linseed oil fatty acids, has a well defined absorption band with maximum absorption at about 968 cm.⁻¹ As an identical band was found in the spectra of fatty acids or esters after isomerization with selenium, it is attributed to the presence of double bonds with a *trans*-configuration. It was found that the same band was present in the spectra of samples taken during hydrogenation of oils, and that its intensity increased to a maximum, then decreased as hydrogenation proceeded. It is concluded that hydrogenation is accompanied by a *cis*-to-*trans* change in some of the double bonds of the fatty acids, and that methyl isolinoleate has at least one double bond with a *trans*-configuration.

Introduction

In the course of an investigation of the hydrogenation of linseed oil, it was found that an isomeric linoleic acid was produced by hydrogenation of linolenic acid (4). Some evidence was presented that indicated that decomposition of isolinoleic acid, as it was called, may be at least partly responsible for the characteristic flavor deterioration of shortening made from hydrogenated linseed oil (4, 5). A method of separating isolinoleic acid in reasonably pure form has also been described (6).

In this paper, the infrared absorption spectra of methyl isolinoleate, of methyl linoleate, of samples taken during the hydrogenation of various vegetable oils, and of oils or esters that have been heated to 200° C. in the presence of selenium will be compared, with reference to an absorption band in the region of 968 cm.⁻¹ that was found in the spectrum of methyl isolinoleate. The significance of this band will be discussed.

Experimental

Methyl isolinoleate was separated from the methyl esters of hydrogenated linseed oil fatty acids by adsorption on silica gel (6). Methyl linoleate was prepared by the method of Rollett (11), and a methyl linoleate concentrate of iodine value 155 was prepared from the fatty acids of sunflower seed oil, after removal of as much as possible of the more saturated acids by crystallization from an acetone solution at -60° C.

In selenium isomerizations, 0.3% selenium powder was used. The oils were heated for three to four hours at 220° C. and were agitated by means of a current of carbon dioxide through the oil.

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Hydrogenations were conducted in a steel pressure vessel already described (4). The oils were alkali refined. A commercial nickel catalyst was used, obtained from the Rufert Chemical Company, Seymour, Connecticut. The catalyst concentration was 0.4% of the weight of the oil. The temperature of hydrogenation was 140° to 150° C., and electrolytic hydrogen at 20 lb. gauge pressure was used. Samples were taken periodically from each hydrogenation for iodine value determinations and infrared absorption measurements.

Iodine values of the samples were determined by the official method of the American Oil Chemists' Society (2).

Some of the samples were separated into solid and liquid acids by the modified Twitchell method of the American Oil Chemists' Society (2). The liquid acids were separated from the filtrates. Both solid and liquid acids were converted to the methyl esters, as the free acids have an absorption band at about 940 cm^{-1} that interferes with measurement of the absorption at the peak of the 968 cm^{-1} band when it is of low intensity.

The infrared absorption curves were obtained with the use of a Perkin-Elmer recording spectrometer. The hydrogenated samples and the methyl esters of the solid and liquid fatty acids were dissolved in carbon disulphide to a concentration of 10%, and cells of 0.1 mm. thickness were used. No solvent was used with the methyl isolinoleate and methyl linoleate samples, and the cell thickness was 0.025 mm.

Results

The chief difference between the infrared absorption spectrum of methyl isolinoleate and that of the two methyl linoleate samples is shown in Fig. 1. The methyl isolinoleate spectrum had a well defined absorption band with maximum at 968 cm^{-1} which was absent in the spectrum of the methyl linoleate concentrate prepared from sunflower seed oil, and was very weak in that of the methyl linoleate prepared by the method of Rollett. No such band was found in the spectra of any of the unhydrogenated vegetable oils examined, but it was present in the spectra of partially hydrogenated samples and in the spectra of oils or esters after heating at 200° C. in the presence of 0.3% selenium for three to four hours.

In Fig. 2 the per cent absorption at the peak of the 968 cm^{-1} band for each hydrogenated sample as compared with the absorption of the unhydrogenated oils at the same frequency is plotted against the iodine value of the sample. In every case the absorption intensity increased to a maximum, then decreased as hydrogenation proceeded. The iodine values at the point of maximum absorption were different for each oil, and were almost directly related to the iodine value of the unhydrogenated oil. The maximum absorption value that developed on hydrogenation was also related to the degree of unsaturation of the unhydrogenated oil, and was considerably greater for linseed and soybean

oils than for those that did not contain linolenic acid. For linseed oil, the iodine value at the point of maximum absorption was approximately the same as that reported previously at which oleic and isolinoleic acids were at a maximum (4).

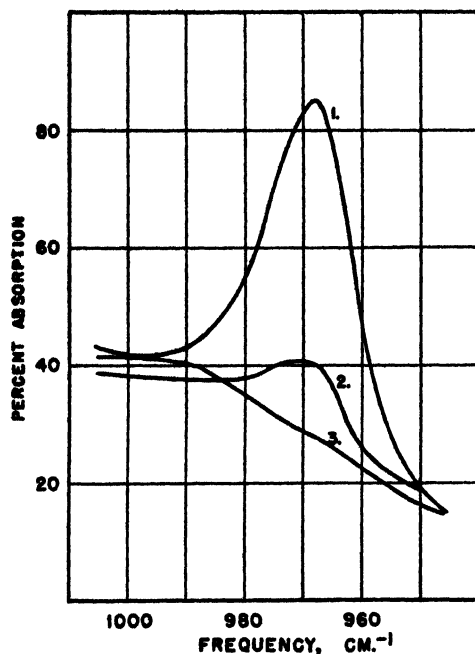


FIG. 1. A portion of the infrared absorption spectra of: 1, Methyl isolinoleate, 2, methyl linoleate prepared by method of Rollett, 3, methyl linoleate concentrate prepared from sunflower seed oil.

The 968 cm.^{-1} band was found in the spectra of the methyl esters of both the solid and liquid fatty acid fractions of hydrogenated peanut oil samples. The per cent absorption values at the peak of the band are given in Table I.

TABLE I

ABSORPTION INTENSITY AT 968 cm.^{-1} FOR METHYL ESTERS OF SOLID AND LIQUID FRACTIONS OF HYDROGENATED PEANUT OIL SAMPLES

Iodine value of sample	Per cent solid acids	Iodine value solid acids	Per cent absorption, methyl esters of solid acids	Iodine value liquid acids	Per cent absorption, methyl esters of liquid acids
80	21	8	12.9	94	18.7
70	27	14	16.8	91	18.7
58	40	20	24.1	85	29.2
39	51	15	23.2	77	35.4
19	72	5	8.8	61	41.1
11	79	3	6.7	46	32.3
6	83	1	6.7	20	20.5
3	85	0.6	6.7	16	12.9

When a mixture of linseed oil and the nickel catalyst was heated at the hydrogenation temperature ($150^{\circ}\text{C}.$) in an atmosphere of nitrogen rather than hydrogen for the length of time required for a hydrogenation, the spectrum showed little trace of the 968 cm.^{-1} band. However, it did appear after very prolonged heating of the oil in the presence of catalyst.

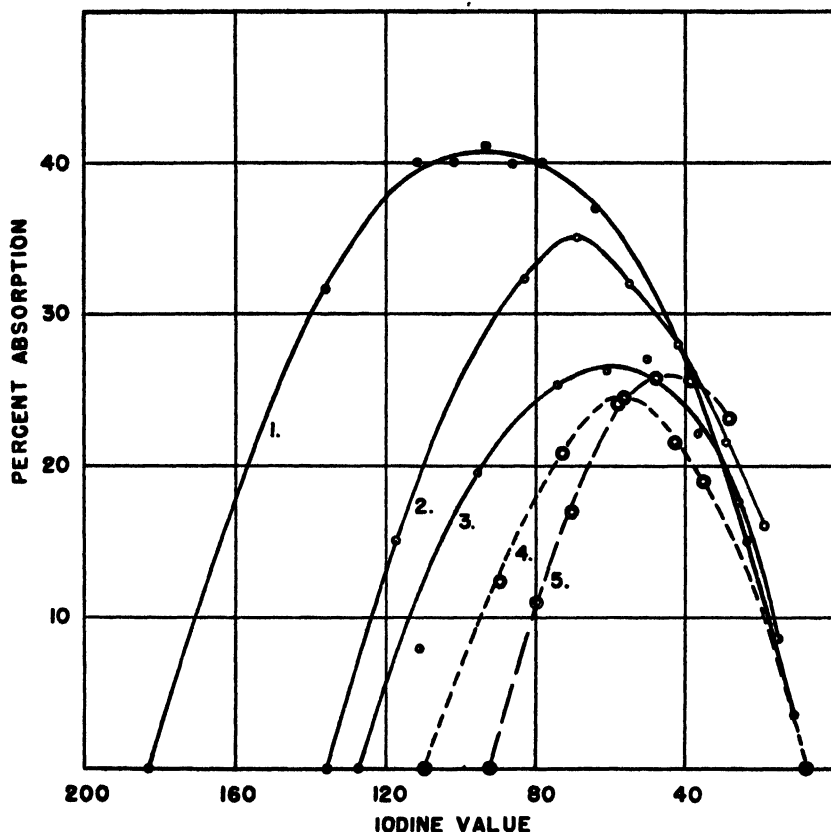


FIG. 2. Effect of hydrogenation on the relation between per cent absorption at the peak of the 968 cm.^{-1} band and iodine value for: 1, linseed oil; 2, soybean oil; 3, corn oil; 4, cottonseed oil; 5, peanut oil.

Discussion

Absorption bands close to 968 cm.^{-1} have been found in the spectra of certain olefins by several investigators. Thompson and Torkington (13) and Thompson and Whiffen (14) have reported that compounds of the type $\text{R}_1\text{—CH=CH—R}_2$, such as butene-2, pentene-2, and octene-2, have an intense absorption band between 960 and 970 cm.^{-1} . They attribute this to deformational motions of the CH bonds contiguous to the double bond. Sheppard and Sutherland (12) have reported absorption bands in this region in the spectra of the products of reaction of certain olefins with hydrogen sulphide. Rasmussen and Brattain (10) have also reported a strong band in this region in the spectra of certain olefins. They have concluded that it is characteristic of the *trans*-form of the CHR=CHR system.

In the case of unsaturated fatty acids, the absorption band at 968 cm^{-1} is apparently also associated with a *trans*-configuration, as the same band is found in the spectra of unsaturated fatty acids, or their esters, after heating for three hours in the presence of 0.3% selenium, which is a well known method of obtaining an equilibrium between *cis*- and *trans*-isomers (3). Rao and Daubert (9) have reported that the infrared spectra of vaccenic and elaidic acids have an absorption band at this frequency, whereas that of oleic acid has not; this was taken as further evidence that vaccenic acid has a *trans*-configuration. It has been reported also that the spectrum of synthetic vaccenic acid has this absorption band (1).

It is concluded, therefore, that the isolinoleic acid produced by hydrogenation of linolenic acid has at least one double bond with a *trans*-configuration. The fact that no increase in the absorption at 968 cm^{-1} resulted when a quantity of methyl isolinoleate was heated in the presence of selenium may mean that both double bonds have a *trans*-configuration.

It is also concluded that the intensity of absorption at the peak of the 968 cm^{-1} band is a measure of the extent of the *cis*-to-*trans* change that is associated with the hydrogenation of unsaturated fatty acids. It was first reported by Moore (8) in 1919 that such a change takes place. He found that the largest component of iso-oleic acid produced on hydrogenation of ethyl oleate was elaidic acid, the *trans*-isomer of oleic acid. He pointed out that the change was an equilibrium reaction, as not only was there a formation of solid elaidic acid on hydrogenation of oleic acid, but also there was a corresponding formation of oleic acid on hydrogenation of elaidic acid.

The fact that the absorption band at 968 cm^{-1} for the liquid acids from hydrogenated peanut oil samples was somewhat more intense than that for the corresponding solid acids indicates that the iso-oleic acid precipitated by the Twitchell method (2) is not the only *trans*-acid that is formed on hydrogenation. It is probable that a considerable proportion of all of the unsaturated acids are *trans*-isomers. What the significance of this may be with regard to the stability or other properties of the products is not at once apparent. It is almost certainly the reason for some of the difficulty that is encountered when the spectral method of fatty acid analysis of Mitchell, Kraybill, and Zscheile (7) is applied to partially hydrogenated oils.

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FLOW PROPERTIES OF DISPERSIONS OF CALCIUM SOAPS IN HYDROCARBON OIL¹

G. B. MOSES AND I. E. PUDDINGTON

Abstract

The flow properties of dispersions of calcium soaps in hydrocarbon oils have been studied over a range of temperature from 35° to 90° C., and rates of shear from 500 to 16,000 sec.⁻¹ by extrusion through a capillary plastometer. The thixotropy of the system falls as the temperature is increased to 50° C. and then rises to a maximum at 65° C., after which it falls regularly. This behavior is due to the thermal weakening of the thixotropic bonds, followed by a strengthening of these bonds due to incipient swelling on the surface of the soap. As the surface of the soap particles continues to swell, cohesion of the particles increases to such an extent that breakdown does not take place and the coefficient of thixotropy falls to very small values. The coefficient of thixotropy found by this method bears a linear relation to the hardness of the dispersion as determined by a falling cone.

Introduction

Lubricating greases are normally stable dispersions of metallic soaps in hydrocarbon lubricating oils. In consistency they may vary from very soft plastic masses to moderately hard solids. Their usefulness in lubrication depends largely on their non-Newtonian flow properties, i.e., the force per unit area necessary to produce continuous flow is not proportional to the rate of shear. They belong to a class of substances which, at constant temperature, show a reversible decrease in apparent viscosity with increasing rate of shear; substances with such properties have been termed thixotropic. The thixotropic properties of greases are responsible for their ability to stay for extended periods in or near the location where lubrication is desired, since at zero rates of shear their viscosity approaches infinity and they do not flow. On the other hand, at high rates of shear the ideal grease should have a viscosity of the same order of magnitude as the oil from which it is made and cause as small a load as possible at the bearings. Greases thus should have the ability to provide good lubrication at high speeds on bearing surfaces and act as self-sealing containers near the edges of the bearings where the rate of shear is low. Oil under similar conditions would flow away from the bearings continuously. Obviously a thorough knowledge of the flow properties of lubricating greases under widely varying conditions of temperature and shear is of prime importance.

The solid phase of conventional lubricating greases is commonly composed of one of the metallic soaps; calcium, sodium, lithium, aluminum, or barium. Each grease possesses individual properties that make it advantageous for some uses but place it at a decided disadvantage for others. Greases containing calcium soaps form the major portion of those in use today, and the results presented here will be confined to that type of grease. These greases are

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unique in that small quantities of water (1 to 3%) are necessary to produce stability in the system although the final product is highly water resistant.

Previous work on the flow properties of greases has been limited to rather narrow ranges of temperature, shear, and composition. Roehner and Robinson (21) determined the apparent viscosities of calcium base greases to show that normal increases in the soap concentration do not necessarily lead to increases in apparent viscosities. Arvison (3, 4) has shown that the apparent viscosity at high shear depends mainly on the mineral oil, the difference from the viscosity of the oil being proportional to the soap content, from which he derives a "soap factor". Beerbower *et al.* (5) showed that the variation of the apparent viscosity with the rate of shear can be used to separate the effect of the soap from that of the oil, and shows each in its proper perspective. Sometimes the reverse of results indicated from cone penetration tests is found by this approach.

Viscosities have been measured (1, 7, 15, 16, 20), by penetration of a double cone, moving parallel plates, rotating cones and cylinders, and capillary type pressure viscometers. Bulkley and Bitner (8) employed a capillary tube type having a cylinder on each end of the tube permitting a series of tests on the same sample of grease by forcing the material in one direction and then reversing the flow.

Experimental

The viscometer used here was of the capillary tube type. A steel cylinder, 7 in. long, $1\frac{1}{2}$ in. outside diameter, and 1 in. inside diameter, having a steel capillary tube screwed into one end and a pressure fitting at the other, was connected through copper tubing, a manifold, and a ballast tank to a nitrogen cylinder. Pressure was supplied by the nitrogen cylinder and measured with a mercury manometer and gauges mounted on the manifold.

The cylinder was filled with grease, care being taken to exclude air pockets, placed in an automatic electrically heated thermostat, consisting of a thick-walled aluminum cylinder, and heated to the required temperature. After the cylinder had been maintained at a single temperature for one hour to allow it to come to equilibrium, samples of the grease were extruded at various pressures, the actual pressure depending on the temperature and soap content of the grease. From the time of extrusion and the weight of the grease extruded, the apparent viscosity and rate of shear were calculated.

The apparent viscosity was calculated from Poiseuille's formula

$$\eta = \frac{\pi r^4 p t}{8 v l},$$

and the value for the reciprocal of the rate of shear from the equation

$$\frac{1}{\sigma} = \frac{\pi r^3 t}{4 v},$$

where all the symbols have their usual meaning.

The greases used were made up from a No. 3 cup grease containing 16.5% of calcium soap and a No. 5 cup grease containing 31.1% of calcium soap, by diluting them with the same oil used in their manufacture. The soap contents were found by ashing and by extraction with chloroform, while the densities of the two basic greases were determined with a dilatometer. Values for the diluted samples were calculated from the known densities of the oil and the concentrated sample. The oil used had the following inspections: viscosity at 100° F., 308 S.U.S.; viscosity index, 74. Temperatures higher than 90° C. were not used because the grease began to separate into two phases and reproducible values for the amount extruded could not be obtained.

The two basic greases used in the work were representative of standard commercial products, the soaps having been prepared from natural glycerides. These were supplied gratuitously by Imperial Oil Ltd., to whom acknowledgment is made.

The radius of the capillary was found to be 0.0368 cm. by weighing the thread of mercury required to fill it, while a length of 2.6111 cm. was obtained using a micrometer caliper. This gives a length-to-diameter ratio of 36 : 1.

The use of a capillary in examining the viscous properties of non-Newtonian materials is often criticized on the grounds that the conditions of shear are not definitely known. However, any device involving concentric cylinders or cones where conditions of shear are known is troublesome to control thermostatically over a wide temperature range, and for this reason capillaries were used in this work. This step appears to have been justified, since values obtained for the apparent viscosity at different rates of shear were essentially the same when the length and radius of the capillary were varied considerably from the one actually used in the major part of this work. Thixotropic equilibrium appears to have been established almost instantaneously at the rates of shear encountered in the capillary.

Results and Discussion

The reproducibility of the experimental results was good. Any inconsistencies could be traced to air pockets or lack of homogeneity in the grease, and these results were discarded. Typical rate of shear vs. shearing stress curves for a range of soap concentrations are shown graphically in Fig. 1.

It is obvious from Fig. 1 that the viscosity of the greases is a function of the rate of shear, and their behavior according to the generally accepted definition, may be termed thixotropic. Thixotropy in systems where the particles of the solid phase are microscopic in size is due to a spontaneous agglomeration of these particles when the system is at rest and a deflocculation of the agglomerates when the system is sheared (2). The addition of small quantities of a third phase that preferentially wets the solid particles has a remarkable effect on the agglomeration. It has been shown (12) by Gallay and Puddington that additions of water greatly increase the equilibrium sedimentation volume and greatly reduce the sedimentation time, for suspensions of a number of solids having hydrophilic surfaces, suspended in

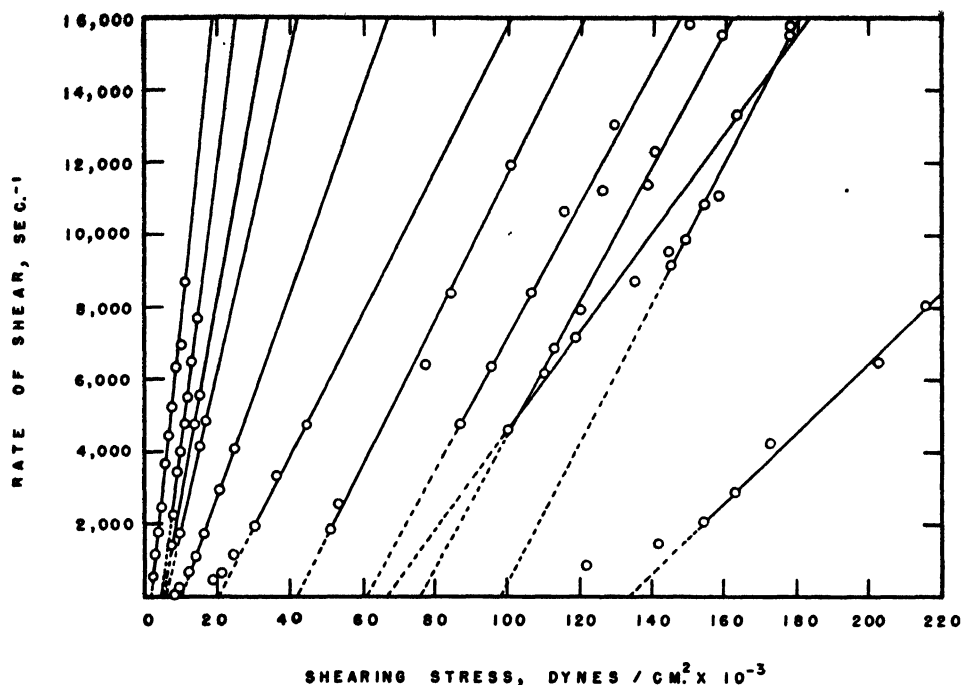


FIG. 1. Change of rate of shear with shearing stress. From right to left, consecutive graphs represent decreasing soap concentration.

organic media. These changes are accompanied by marked viscosity changes. Kruyt and van Selms (17) have shown that the same behavior is observed if small quantities of hydrocarbons are added to finely divided coal suspended in water. It is also probable that particle shape plays an important part in this phenomenon.

Goodeve (14) has advanced the theory, based on this conception of thixotropy, that under conditions of uniform shear, an equilibrium should be established where the rate of deflocculation due to shear should be equal to the rate of spontaneous agglomeration, and has derived the following formula relating viscosity and shear.

$$\eta - \eta_0 = \frac{\theta}{\sigma}$$

where η = the apparent viscosity of the system,

η_0 = the residual viscosity

σ = shear

θ = the coefficient of thixotropy.

Obviously if a system conforms with this equation a plot of η vs. $\frac{1}{\sigma}$ should give a straight line. This was found to be the case, at high rates of shear, for a number of systems, and the coefficient of thixotropy, θ , is defined by the limiting slope of the viscosity - reciprocal shear curve. Extrapolation of this curve to $\frac{1}{\sigma} = 0$ gives the value for the residual viscosity, i.e., the viscosity

of the suspension where no agglomerates exist and the solid phase particles are independent of one another.

The experimental results in the present work have been examined on the basis of Goodeve's theory. Typical data are presented graphically in Fig. 2,

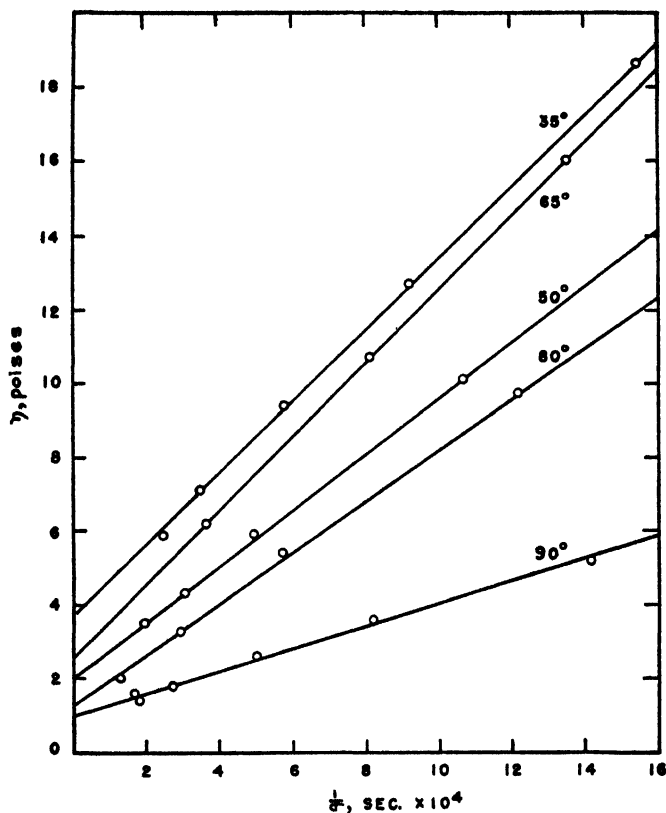


FIG. 2. Change in apparent viscosity with the reciprocal of the rate of shear for grease containing 16.5% of soap.

where the apparent viscosity in poises is plotted against the reciprocal shear (seconds) for a single soap concentration at five different temperatures. In all, the flow characteristics were measured* and the data plotted in this manner for 11 different soap concentrations. The tabulated results are shown in Table I, where values of both the residual viscosity, η_0 , and the coefficient of thixotropy, θ , are recorded for the different temperatures.

Although the system was examined in detail at rates of shear up to 16,000 sec.^{-1} , in a few experiments this range was extended to 220,000 sec.^{-1} without any significant change in the results presented here.

The variation of the coefficient of thixotropy with temperature is shown in Fig. 3. At all concentrations below 27% of soap the values of θ fall to a minimum at 50°C. followed by a rise to a maximum at 65°C., after which the value decreases regularly and the indications are that it would reach zero in the vicinity of 100°C. Actually this point could not be checked

TABLE I

EXPERIMENTAL VALUES OF θ AND η_0 FOR DISPERSIONS OF CALCIUM SOAPS IN HYDROCARBON OILS

Temp., °C.		35°	50°	65°	80°	90°
% Soap	θ					
	η_0					
11	θ	4300	3650	2300	1800	1200
	η_0	1.28	0.57	0.44	0.33	0.24
13	θ	5600	4200	3800	2800	1550
	η_0	1.63	0.91	0.54	0.23	0.24
14	θ	6100	5300	4500	3500	2100
	η_0	2.20	1.03	1.12	0.47	0.28
16.5	θ	9700	7600	10100	7200	2800
	η_0	3.7	2.0	2.5	1.2	1.0
18	θ	22000	17900	21000	12400	4500
	η_0	4.35	2.8	2.8	1.5	1.1
22	θ	44200	32400	33600	17900	12250
	η_0	4.8	3.5	4.2	2.5	1.4
25	θ	60700	47000	50000	31000	17500
	η_0	5.5	3.0	2.1	1.85	1.65
26	θ	74200	53300	56700	33500	18600
	η_0	5.9	4.0	3.3	3.1	2.6
27	θ	82100	62300	62300	42700	28500
	η_0	6.3	3.8	3.8	3.0	1.9
29	θ	119700	77200	73400	59800	32750
	η_0	3.6	4.9	2.7	2.65	2.15
31.1%	θ	145200	135000	107000	77300	52500
	η_0	8.7	4.3	5.9	2.9	1.7

 θ , dynes per cm.² η_0 , poises.

experimentally, as the grease started to separate at temperatures above 90° C. and the viscosity readings were unreliable.

The marked decrease in θ is surprising in view of the fact that Arnold and Goodeve found an extremely small temperature coefficient with carbon black in oil. However, the temperature range here is larger and the volume concentration of solid phase much higher than those used by Goodeve. Further, this system contains water, while the carbon black in oil was essentially

anhydrous. Kruyt and van Selms (17, 18) have recently pointed out that plasticity in many suspensions containing small amounts of a third phase can be accounted for on the basis of the interfacial surface tension of the

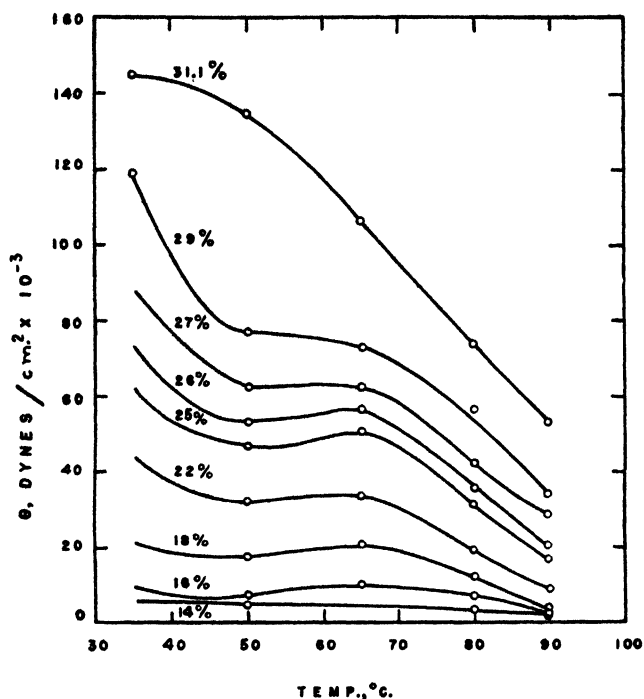


FIG. 3. Change in the coefficient of thixotropy with temperature at different soap concentrations.

third phase, which actually forms liquid bridges between the individual particles of the suspension, against the liquid medium of the suspension. An explanation of this sort would necessitate a reduction in the coefficient of thixotropy with increasing temperature, proportional to the product of the surface tension lowering and the number of bonds present. In the present instance the lowering of θ is proportional to the concentration of the solid phase (Fig. 4), a result to be expected from the above consideration.

The increase in θ following the minimum at 50° C. is probably due to incipient swelling of the surface of the soap particles, which produces considerable adhesion when the soap particles come in contact, and a change in the mechanism of thixotropy. This adhesion would be expected to increase with rising temperature to a point where the shear produced under the experimental setup would no longer be able to disintegrate the agglomerates, and the value of θ would go through a maximum and fall toward zero. Under these conditions the solid phase would form a clot and the liquid might be lost by syneresis, or the system remain in a highly swollen condition. Actually with calcium base greases of these concentrations the former usually occurs.

It is quite likely that thixotropy in these systems is a combination of the natural tendency of the soap particles to agglomerate owing to their polarity

and the bridging effect of the added water. At low temperatures the effect of the water predominates, while above 50° C. the incipient swelling of the soap causes the natural adhesion to become more pronounced. This swelling

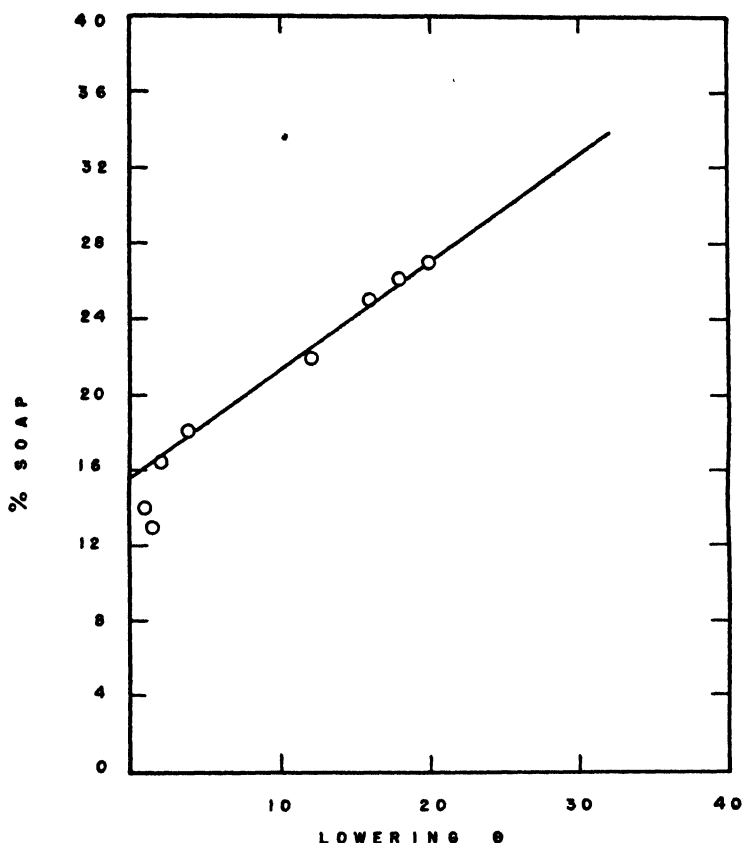


FIG. 4. Change in the lowering of the coefficient of thixotropy between 35° and 50° C. with soap concentration.

phenomenon may not attain equilibrium quickly nor is it likely to be strictly reversible, since temperature gradients are usually important in this sort of change. Obviously, it has been found of considerable practical importance, since lime base greases of this type are never recommended for use at temperatures exceeding 60° C. In support of this incipient swelling hypothesis, it was noted experimentally that a sample of soap from which most of the oil was removed became noticeably sticky at 50° to 60° C.

At high concentrations of soap (31.1%) no marked loss in the thixotropy was noted until temperatures higher than 50° C. were reached. At concentrations as high as this it is probable that disintegrated agglomerates must re-form as soon as shearing forces decrease, since the concentration is sufficiently high that each soap particle is in contact with its neighbors and the increased bond strength due to the presence of water has little effect on the size of the agglomerates formed, and hence on θ . When the temperature is

impact range. It did depend on the cone angle however, and Cameron decided that a 90° cone gave results that represented the grease hardness accurately.

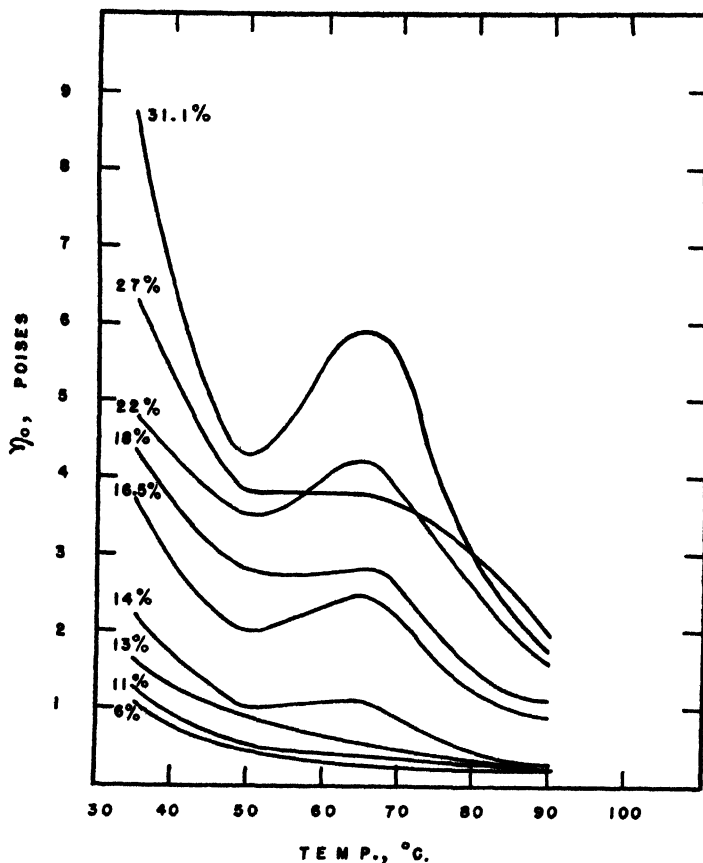


FIG. 6. Change in residual viscosity with temperature at different soap concentrations.

Since there should be a relation between hardness and the yield value of a grease as defined by Bingham (6), i.e., the shearing force per unit area necessary to overcome the internal elastic stress, the yield values of the present series of greases were determined by extrapolating the linear portions of the rate of shear vs. shearing stress curves, shown in Fig. 1, to zero rate of shear. The hardness values were determined as described by Cameron, using a 90° hollow cone with a 6 cm. slant height having a light graduated rod attached to the open end. The assembly weighed 78 gm. Extra weights were added to give penetrations of at least 10 mm. The assembly was allowed to fall from 5 to 25 cm.

Cameron's results were confirmed to the extent that the hardness of the grease was constant over the range of impact energies used up to a soap concentration of 25%. In Table II the hardness values are compared with the Bingham yield values and the coefficients of thixotropy.

TABLE II
COMPARISON OF HARDNESS AND THIXOTROPY OF GREASES

% Soap	H , dynes/cm. ²	θ , dynes/cm. ²	Yield value, dynes/cm. ²
13	25.1	5.6	5.0
14	26.6	6.1	5.5
16.5	49.4	9.7	10.0
18	71.8	22.0	20.2
22	113	44.2	41.7
26	149	74.2	76.0
31.1	406	145.2	133.5

The absolute values of the yield values agree well with coefficients of thixotropy, any difference probably being due to extrapolation error. This is to be expected since the Goodeve and Bingham equations are identical, with the exception of the difference in meaning attached to θ . Both may be expressed in dynes per square centimeter.

When the values in Table II are plotted (Fig. 7), the relation is approximately linear with $H = 20 + 2\theta$. This relation changes somewhat with cone

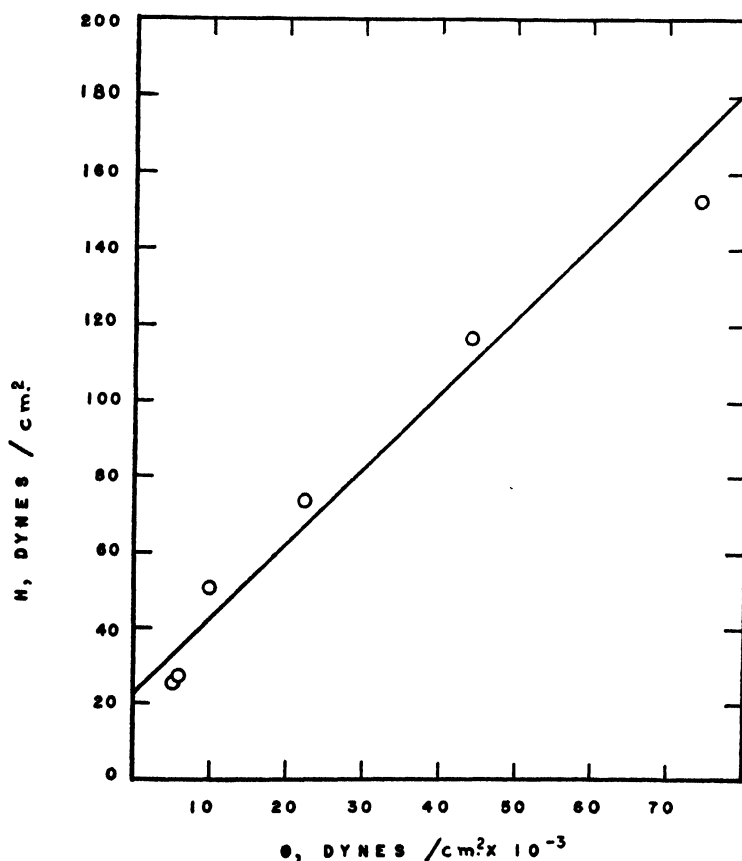


FIG. 7. Comparison of hardness and the coefficient of thixotropy.

angle and it might be possible to produce a cone that would give closer absolute values. It is also probable that this value depends on the particle shape of the solid phase and may have a different relation for other types of grease.

In grading lubricating greases the degree of thixotropy or yield value is of much more importance than the viscosity or mobility, since the latter property is controlled largely by the viscosity of the oil used in its manufacture. The usefulness of the finished product depends principally on the coefficient of thixotropy. The hardness test described by Cameron offers a rapid method of estimating this property and gives a result that is more clear-cut scientifically than the double cone penetrometer test commonly used today.

The results of the present investigation illustrate clearly that the short-coming of calcium base lubricating greases is due to an interaction between the soap and oil at a relatively low temperature, which seriously alters the flow characteristics, causing an increase in the apparent viscosity and almost complete loss of thixotropy. This change is not usually reversible and the value of the grease as a lubricant is greatly diminished. Previous investigations here and elsewhere (13, 22) would suggest that this is due to a phase change in the soap and does not depend on the oil used during the manufacture.

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THE USE OF P^{32} LABELED GLYCEROPHOSPHATE IN THE STUDY OF YOLK PHOSPHOLIPIDS¹

BY J. W. T. SPINKS, C. C. LEE, AND J. B. O'NEIL

Abstract

Labeled sodium glycerophosphate has been prepared by phosphorylating glycerol with sodium dihydrogen phosphate containing P^{32} . After the labeled sodium glycerophosphate had been fed to a laying hen, radiophosphorus from glycerophosphate appeared in the shells, whites, and yolks of the eggs. The uptake in different eggs followed a pattern similar to that found for inorganic phosphate, the maximum occurring at the fourth or fifth egg. Comparative studies using P^{32} labeled sodium glycerophosphate and trisodium phosphate indicate that the rate of utilization of the phosphorus from glycerophosphate is less than the rate of utilization of the phosphorus from inorganic phosphate. The possibility of an enzymatic hydrolysis of glycerophosphate followed by the incorporation of the resulting phosphoric acid into the phospholipids and the phosphorylation of lower glycerides (partially hydrolyzed fat) by inorganic phosphate as a mechanism for phospholipid formation is discussed.

Introduction

The incorporation of phosphorus from inorganic phosphate into yolk phospholipids was first demonstrated by Hevesy and Hahn (14), and by Entenman *et al.* (9), through the injection of P^{32} labeled sodium phosphate into hens. It was concluded that the phospholipids are formed in the liver and carried by the blood plasma to the ovary, where their deposition in the yolks takes place (14). In 1942, Chargaff (6) administered P^{32} to hens by intramuscular injection of sodium phosphate, and then determined the specific activity of the phosphorus in the free and bound (with lipoproteins) lecithin and cephalin, the vitellin, and the acid soluble fraction from the yolks of eggs laid in the course of eight days following the injection. P^{32} containing ovovitellin prepared in this way has recently been applied by Francis and Wormald (12) to the immunological investigation of the vitellin-antivitellin precipitin reaction. Further applications of P^{32} in the study of hens' eggs has been reported by Lorenz *et al.* (16), who determined the per cent uptake of radiophosphorus in a large number of eggs from hens after injection of labeled sodium phosphate, and by O'Neil *et al.* (17), who determined the uptake of phosphorus in the shells, whites, and yolks of eggs from hens that received a diet in which the bone meal was replaced by calcium phosphate containing P^{32} .

In a review on phospholipid metabolism, Chaikoff (4) pointed out that consideration of the structural formulae suggests that glycerophosphate might act as intermediate in the formation of the phospholipids, lecithin and cephalin. The observation of Flock and Bollman (11) that the specific activity of glycerophosphate, isolated from cock livers after administration of P^{32} labeled sodium phosphate, was higher than that of the phospholipids and lower than that of

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inorganic phosphate from these livers is suggestive of such an intermediary role for glycerophosphate. Moreover, Zilversmit *et al.* (24) have, very recently, presented evidence to indicate that, after injection of inorganic phosphate into dogs, the specific activity of dog liver alkali-stable phosphorus, which was found to be rich in glycerophosphate, satisfied the criteria for a precursor of dog liver lecithin. No comprehensive study of the metabolic relationship between glycerophosphate and the phospholipids by the direct use of labeled glycerophosphate has, so far, been reported in the literature. Although Taurog and Chaikoff (4, 23) have isolated P^{32} labeled glycerophosphate from radioactive rat liver phosphatides and found that the activity from glycerophosphate did incorporate into the phospholipids of rat liver and kidney *in vitro* and *in vivo*, it was uncertain whether a breakdown of the glycerophosphate to inorganic phosphate occurred before the incorporation of the radiophosphorus into the phospholipids. The procedure for Taurog's method of preparation of labeled glycerophosphate was recently reported by Zilversmit *et al.* (24).

P^{32} labeled α -glycerophosphate has been prepared by Chargaff (5) according to the method of Fischer and Pfähler (10), which involved the treatment of isopropylidene glycerol with phosphoryl chloride containing P^{32} . Since P^{32} is generally obtained in the form of inorganic phosphate, a much simpler method is afforded by the well known commercial procedure for the preparation of glycerophosphate from glycerol and sodium dihydrogen phosphate (19). King and Pyman (15) have studied the constitution of this compound and concluded that it is the β isomer. Crystalline disodium glycerophosphate (crystallized from alcohol and water) has been prepared in this laboratory according to this procedure. It melted in the same range (85° to 95° C.) as the commercially obtained mixtures of α - and β -sodium glycerophosphate. It is therefore unlikely that the product is of the pure β form, although the β isomer may be the predominant one in the mixture of α - and β -sodium glycerophosphate we prepared. It was also found that a better yield was obtained when the product was isolated as barium glycerophosphate. The present report deals with experiments in which laying hens were given P^{32} labeled disodium glycerophosphate prepared by the phosphorylation of glycerol with radioactive sodium dihydrogen phosphate. Some of the hens were also given P^{32} labeled trisodium phosphate after the glycerophosphate activity had decayed to a negligible amount. A comparison of the utilization of phosphorus from glycerophosphate and inorganic phosphate in the formation of yolk phospholipids is thus possible.

Experimental

Synthesis of Glycerophosphate

Sodium dihydrogen phosphate (1.18 gm.) containing 76,900 registers per minute* of P^{32} activity was heated with 3 cc. of glycerol under reduced pressure

* One register per minute on the mechanical counter is equal to 128 radioactive disintegrations counted. The actual number of beta disintegrations is equal to the number of counts multiplied by a factor of 3.9 (counter efficiency was measured using a RaD-RaE standard from the National Bureau of Standards, Washington).

at 180° to 190° C. for two hours. The resulting mixture was refluxed for two hours with 20 cc. of 10% sodium hydroxide solution and then a barium chloride solution was added to precipitate all unreacted inorganic phosphate. Following the removal of the barium phosphate, it was found that some of the barium glycerophosphate could be precipitated out by bringing the solution to boiling. However, a more complete recovery of the glycerophosphate was effected by the method of Rae (20), which involved the precipitation of lead glycerophosphate, the decomposition of the lead salt with hydrogen sulphide, the removal of lead sulphide and excess hydrogen sulphide, the neutralization of glycerophosphoric acid with barium hydroxide, and then the precipitation of barium glycerophosphate with alcohol. The yield based on the P^{32} activity was 65.3%.

Analysis $C_3H_7O_6P\text{Ba}$ requires $P = 10.08\%$. Found $P = 9.85\%$.

For the experiments described below, weighed amounts of barium glycerophosphate were dissolved in water and the barium ions were removed by precipitation with equivalent amounts of sodium sulphate.

One of the main sources of phosphorus in the laying mash fed to our experimental birds is the bone meal, which contains about 140 mgm. of phosphorus in a single day's feed. To make it possible to compare the results of the present experiments with those of previous experiments with calcium phosphate (17), it was decided to replace the bone meal with sodium glycerophosphate and to administer to each hen an amount (active + inactive) equivalent to 140 mgm. of phosphorus.

Experiment A

A solution of sodium glycerophosphate, containing 140 mgm. of phosphorus with 3510 reg. per min. of P^{32} activity (0.79 microcurie) on the day of feeding, was mixed with the laying mash and fed to a Barred Plymouth Rock Pullet (Hen No. 1). Eighteen eggs laid subsequent to the feeding were separated into shells, whites, and yolks, then wet ashed with nitric and perchloric acid and analyzed for total activity according to the method of O'Neil *et al.* (17).

Experiment B

Two Barred Plymouth Rock Pullets (Hens No. 2 and 3) were isolated for this experiment. Each of these birds received 11 cc. of sodium glycerophosphate solution containing 140 mgm. of phosphorus with 7260 reg. per min. of P^{32} activity (1.63 microcurie) on the day of administration. This solution was injected subcutaneously into Hen No. 2 and was fed in a single feeding of laying mash to Hen No. 3. Each of the yolks of eggs No. 2, 3, 4, 5, 6 of both hens laid subsequent to the administration of the activity was dispersed in 100 cc. of 10% sodium chloride solution. A 10 cc. aliquot was wet ashed for determination of total activity. The remainder was extracted with three 80 cc. portions of ether, and the free (not bound to the lipoproteins) lecithin and cephalin fractions were isolated according to the method of Chargaff (6). The precipitated free lecithin and cephalin fractions were also wet ashed for determination of radioactivity. Appropriate aliquots of all ash solutions

were reserved for colorimetric determination of total phosphorus according to the method of Shelton and Harper (22).

Six 24 hr. samples of droppings from each hen were collected after the administration of the activity. These droppings were dried by hot air and then pulverized. To a representative 10 gm. aliquot, 200 cc. of distilled water was added and the mixture was allowed to sit overnight. The supernatant solution was then separated by centrifuge, and the residue washed thoroughly with distilled water. To the combined water extract and washings, barium chloride solution was added to precipitate the water soluble inorganic phosphates. Where necessary, ammonium hydroxide was added to render the solution slightly basic in order to get complete precipitation. This barium precipitate is called fraction A. It contains all water soluble inorganic phosphates. The filtrate from the barium precipitate is called fraction B. It contains all water soluble glycerophosphates. The residue from the original water extraction is called fraction C. It contains all water insoluble phosphorus compounds. After wet ashing, the radioactivity and total phosphorus of all fractions were determined.

Experiment C

Eighty days after the administration of labeled sodium glycerophosphate, it was found that the eggs of the hens used showed negligible activity. Hens No. 2 and 3 were then each given 10 cc. of trisodium phosphate solution containing 140 mgm. of phosphorus with 8280 reg. per min. of P^{32} activity (1.86 microcuries) on the day of administration. As in Experiment B, Hen No. 2 received the solution by subcutaneous injection and Hen No. 3 by feeding. The yolks of eggs subsequently laid were analyzed as in Expt. B.

Results

The results from Expt. A, expressed as % uptake of P^{32} , are shown by histogram in Fig. 1.

The activity per milligram of phosphorus for all the fractions from Expts. B and C can be calculated. This specific activity can be expressed as per cent of the initial specific activity, thus making possible the comparison of the results of experiments involving different amounts of radioactivity. The initial specific activity in these experiments is the activity administered to each hen divided by 140, the number of milligrams of phosphorus each hen received. The results are compared graphically in Figs. 2 and 3. It will be noted that our data may be made to agree with Chargaff's (6) if one assumes that in Chargaff's experiment each hen also received 140 mgm. of phosphorus in the feed.

Since the total activity of each yolk from Expts. B and C was determined, the total uptake of P^{32} can also be calculated. Results of these calculations are shown in Fig. 4.

Results of the determination of radioactivity in the droppings from Expt. B, expressed as per cent of P^{32} excreted, are tabulated in Table I.

TABLE I
EXCRETION OF P^{32} AFTER ADMINISTRATION OF SODIUM GLYCEROPHOSPHATE
SIX 24 HR. SAMPLES FROM EACH HEN

Sample No.	Fraction	Hen No. 2—Activity injected		Hen No. 3—Activity fed	
		% of P^{32} excreted	Total P, mgm.	% of P^{32} excreted	Total P, mgm.
1	A	16.40	191	16.68	201
	B	0.31	7.5	0.47	3.6
	C	8.75	243	9.56	198
2	A	3.74	198	4.53	231
	B	0.18	8.6	0.16	8.5
	C	1.19	209	2.12	193
3	A	0.95	193	1.78	116
	B	0.06	5.7	0.11	3.2
	C	0.87	171	1.27	182
4	A	0.82	204	1.00	160
	B	0.06	15.5	0.13	10.4
	C	0.94	292	0.53	279
5	A	1.06	143	0.45	210
	B	0.06	12.8	0.05	10.5
	C	0.63	362	0.38	274
6	A	0.84	166	0.09	48
	B	0.08	15.8	0.03	5.1
	C	0.28	234	0.04	227

Fraction A was water soluble and the activity was precipitated by barium ions.
Fraction B was water soluble but the activity was not precipitated by barium ions.
Fraction C was water insoluble.

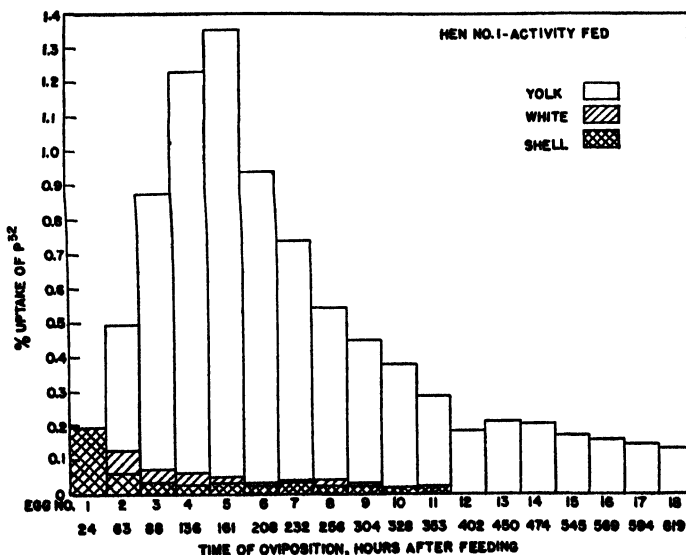


FIG. 1. Percentage uptake of P^{32} in successive eggs laid after feeding hen No. 1. with sodium glycerophosphate containing P^{32} .

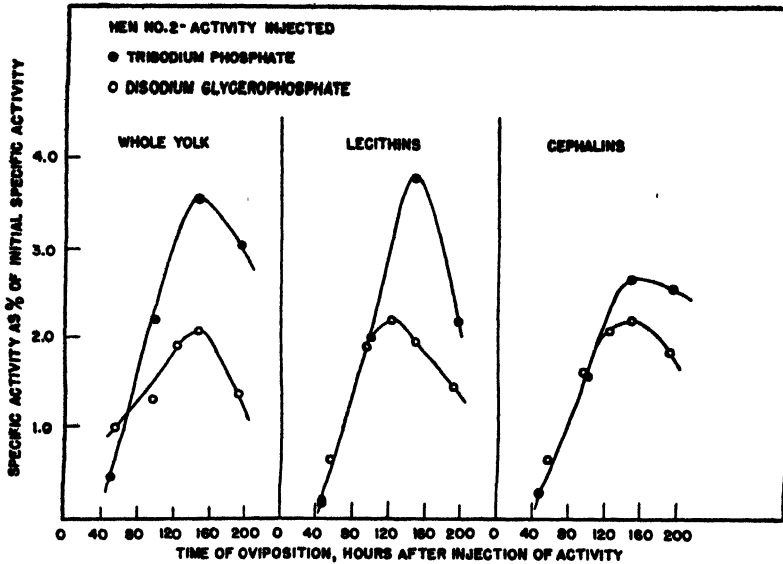


FIG. 2. Specific activities of whole yolk, lecithin, and cephalin from eggs of hen No. 2 injected (a) with sodium glycerophosphate and (b) eighty days later with sodium phosphate.

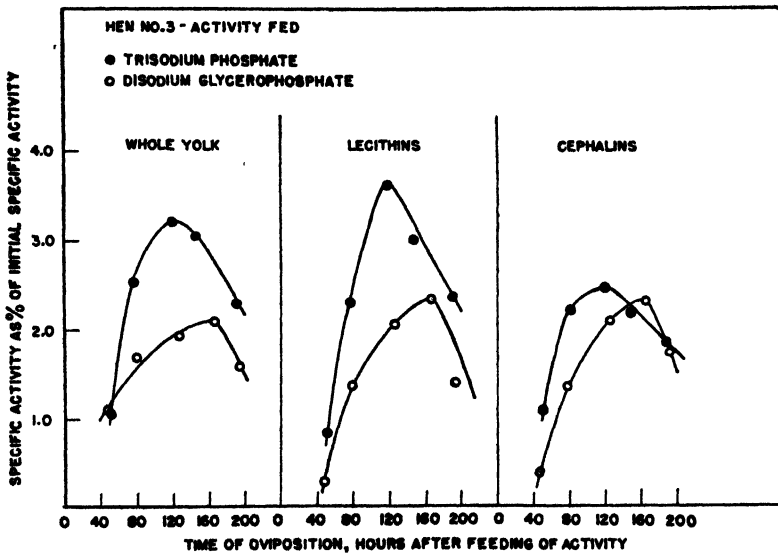


FIG. 3. Specific activities of whole yolk, lecithin, and cephalin from eggs of hen No. 3 fed (a) with sodium glycerophosphate and (b) eighty days later with sodium phosphate.

Discussion

It can be seen from Fig. 2 that the initial parts of the specific activity - time curves for the lecithin and cephalin fractions for trisodium phosphate and sodium glycerophosphate, administered by injection, coincided. In Fig. 3, where the data are from experiments in which the activities were administered by feeding, no such coincidence occurred. These variations may be due to individual differences of the experimental birds. With the limited number of

data, no significant conclusions can be drawn regarding the differences, if any, that arise from the different methods (injection and feeding) of administration of the labeled compound.

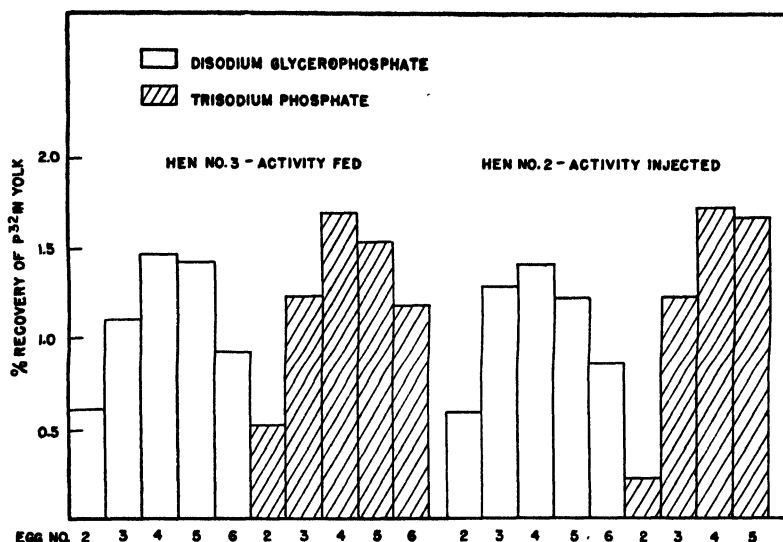


FIG. 4. Percentage recovery of P^{32} in yolks for hens No. 2 and 3 injected and fed, respectively, with sodium phosphate and sodium glycerophosphate.

A plot of specific activity against time is indicative of the rate of utilization of the phosphorus from the compound in question. Figs. 2 and 3 show that after administration of inorganic phosphate the maximum specific activities of the phosphorus in the whole yolk, lecithin, and cephalin fractions are higher than the corresponding maximum specific activities after administration of glycerophosphate. The total uptake of radiophosphorus from inorganic phosphate is also greater than the total uptake of radiophosphorus from glycerophosphate, as may be seen in Fig. 4. These results would seem to indicate that in the formation of yolk phospholipids, the rate of utilization of phosphorus from glycerophosphate is less than the rate of utilization of phosphorus from inorganic phosphate. The fact that after administration of glycerophosphate very little water soluble glycerophosphate was excreted as such (Table I) indicates that the bulk of the glycerophosphate was hydrolyzed before excretion. It is, of course, possible that the incorporation of the phosphorus from glycerophosphate into phospholipids results from the use of the phosphoric acid after the glycerophosphate is enzymatically hydrolyzed. However, these experiments provide no positive evidence on this point. Experiments with glycerophosphate labeled with both C^{14} and P^{32} would afford more conclusive proof as to whether this compound is hydrolyzed before utilization in the biosynthesis of phospholipids.*

* In view of the possible difference in rates of utilization of the α and β isomers, experiments with the pure isomers (including optically active ones) would also be of interest.

It is of some interest to note that experiments by other workers using P^{32} labeled phosphoryl ethanolamine (7) and phosphoryl choline (21) indicated that these esters are not used directly in phospholipid formation. Recently, Frazer and Sammons (13) obtained evidence indicating that fats are absorbed as lower glycerides (mono and di) and tentatively suggested that these lower glycerides form the basis for phospholipid synthesis. It could perhaps be further suggested that phosphorylation of the lower glycerides can be effected only by inorganic phosphate. In that case, the phosphorus from esters such as glycerophosphate, phosphoryl choline, and phosphoryl ethanolamine would be used by the animal for phospholipid synthesis only after hydrolysis to phosphoric acid. Reaction between a phosphorylated diglyceride and the nitrogen containing base would then give rise to the phospholipid molecule. Such a mechanism would account for the observation that ethanolamine and its products of partial methylation (2) as well as choline (1, 8, 18) stimulated the utilization of radiophosphorus from injected inorganic phosphate for phospholipid formation while, on the other hand, the utilization of radiophosphorus from labeled phosphoryl ethanolamine (7) and phosphoryl choline (21) was not as great as that from inorganic phosphate. Furthermore, it has been observed that the rate of formation of rat liver phospholipids was increased by a fat-rich diet (3). The stimulating effect of choline on lipid phosphorylation was also found to be enhanced by simultaneous ingestion of a large amount of fat (1). Such observations can be attributed to a greater availability of lower glycerides from a fat-rich diet if these lower glycerides were involved in phospholipid formation as required by the mechanism suggested above. The findings of Flock and Bollman (11) and Zilvermit *et al.* (24) can also be reconciled to the suggested mechanism of phospholipid formation if the glycerophosphate fractions obtained by these workers were derived from phosphorylated lower glycerides.

Conclusion

Studies using P^{32} labeled sodium glycerophosphate and sodium phosphate indicate that the rate of utilization of the phosphorus from glycerophosphate is less than the rate of utilization of the phosphorus from inorganic phosphate. To account for this and other observations reported in the literature, it is suggested that organic phosphate esters are not used directly in phospholipid formation. They may, however, be first hydrolyzed enzymatically and the resulting phosphoric acid may then be incorporated into the phospholipid molecule. The phosphorylation of lower glycerides (partially hydrolyzed fats) solely by inorganic phosphate is tentatively suggested as an essential step in the biosynthesis of the phospholipids, lecithin and cephalin.

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SOLUBILITY OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN ORGANIC SOLVENTS AT 20° C.¹

BY L. YAFFE²

Abstract

A study has been made of the solubility of uranyl nitrate hexahydrate and thorium nitrate tetrahydrate in various organic solvents at 20° C. In all the solvents investigated no case was found where the thorium nitrate tetrahydrate was more soluble than the uranyl nitrate hexahydrate. Hydrocarbons do not dissolve either compound to an appreciable extent. Addition of a ketone, aldehyde, or alcohol group enhances the solubility considerably. The simpler the compound the greater the solubility of the nitrate in any given family.

Introduction

In order to establish a general relationship between the solubilities of the nitrates of some of the heavier elements in organic solvents and the molecular constitution of the solvent, and to supplement the very meager quantitative data existing, a comprehensive survey of the solubilities of uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and thorium nitrate tetrahydrate, $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, was made in organic solvents that were available. At the time this work was undertaken no such data were available.

Wells (10) measured the solubility of thorium nitrate in ether to determine whether Hillebrand's (3) method of dissolving uranyl nitrate in ether in order to remove last traces of rare earths was applicable in this case. Misciattelli (6) measured the solubilities of uranyl nitrate and thorium nitrate in ether. In order to get data about the quaternary system uranyl nitrate - thorium nitrate - ether - water Misciattelli (7, 8) also studied the two ternary systems, uranyl nitrate - ether - water and thorium nitrate - ether - water. Imre (4, 5) extracted thorium nitrate from aqueous solution using ether. Mlle O. Guempel (2) also studied the system uranyl nitrate - ether - water. Gmelin (1) lists qualitative data regarding a few solvents in which uranyl nitrate is soluble. Templeton and Hall (9) have recently published a comprehensive survey of the solubility of thorium nitrate tetrahydrate at 25° C.

Experimental

(a) Materials

Thorium nitrate tetrahydrate Bakers C.P. analyzed was used in all cases. Uranyl nitrate hexahydrate was obtained from the Eldorado Mining and Refining Co. The maximum impurities consisted of rare earths (<0.1%). The organic solvents used were "practical" grade or better.

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Contribution from the Montreal Laboratories of the National Research Council of Canada. Issued as N.R.C. No. 1960. The work described in this paper was completed and reported as MC-116 Feb. 15, 1945, but could not be released for publication at that time owing to security regulations.

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(b) Method

Twenty-five cubic centimeters of the solvent was used in each case. To this volume in a 50 cc. centrifuge tube was added a few grams of thorium nitrate tetrahydrate or uranyl nitrate hexahydrate. The tube was then sealed and agitated in "end-over-end" fashion in a water bath thermostatically controlled at $20^{\circ}\text{C.} \pm 0.5^{\circ}$. More solid was added if necessary until a saturated solution was obtained. The minimum time for saturation to occur was taken to be 24 hr. Some samples were agitated for four days before saturation was complete. Some samples showed a discoloration that was probably due to solvent decomposition. In order to ensure that true equilibrium existed, several solvents that did not decompose were tested at higher temperatures and allowed to cool down to 20°C. Analysis of the solution showed good agreement between results obtained by agitation at 20°C. and by approaching the equilibrium from a higher temperature. Before analysis, the solution was centrifuged to remove any of the solid that might have been present in the form of a suspension.

To analyze for thorium, an aliquot of the solvent layer was pipetted off, the solvent evaporated off, and the residue ignited to thorium oxide.

The uranyl nitrate was back-extracted into water and the concentration determined colorimetrically. The solution was diluted sufficiently so that the concentration was in the range where Beer's law held. Results of these analyses were checked using U^{233} as tracer. The samples were counted using an ionization chamber and linear amplifier (11) and were found to agree with the colorimetric analyses to within $\pm 5\%$ and all analyses are quoted to within that figure.

Results

The solubilities of uranyl nitrate hexahydrate and thorium nitrate tetrahydrate in various ethers is given in Table I. The results are shown graphically in Fig. 1 where the change in solubility with increasing number of carbon atoms is plotted for straight chain aliphatic ethers.

In Table II and Fig. 2 are shown the results for alcohols, with a graphical representation of the solubility in straight chain aliphatic alcohols.

In Table III are shown the solubilities in the various esters. In Fig. 3 is shown the variation of the solubility of uranyl nitrate hexahydrate and thorium nitrate in various acetates with increasing number of carbon atoms. The results for homologous series of amyl esters are also plotted.

Tables IV, V, VI, VII list the results of the solubilities in various ketones, aldehydes, hydrocarbons, and substituted hydrocarbons respectively.

Some generalizations may be drawn from the data presented.

1. In all the solvents examined, where solubility could be measured, no case has been found where the solubility of thorium nitrate tetrahydrate in a selected solvent is greater than that of uranyl nitrate hexahydrate.
2. Hydrocarbons do not dissolve either compound to any appreciable extent.

TABLE I

SOLUBILITY OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS ETHERS AT 20° C. IN ORDER OF DECREASING SOLUBILITY

Solvent	UO ₂ (NO ₃) ₂ · 6H ₂ O, gm. per 100 cc. of solvent	Th(NO ₃) ₄ · 4H ₂ O, gm. per 100 cc. of solvent
Diethylcellosolve	102	6.8
Dimethyldioxane	92	30.0
Diethyl ether	74	17.0
Ethylhexylcellosolve	68	6.9
Dibutylcellosolve	49	6.4
Dibutylcarbitol	44	8.8
Pelargonic ether	17	—
<i>n</i> -Butyl ether	16	—
Xanthyl ether	14	—
Amyl ether	11	.02
Hexyl ether	9	0.08
Isopropyl ether	9	—
Dichloroisopropyl ether	5	0.4
Isoamyl ether	<0.1	<0.1
Amylphenyl ether	"	"
<i>p</i> - <i>tert</i> -Amylphenyl methyl ether	"	"
β -Bromoethyl ethyl ether	"	"
γ -Bromopropyl phenyl ether	"	"
Methyl phenyl ether	"	"
<i>o</i> -Chloroisopropyl ether	"	"
2-Chloro-4- <i>tert</i> -amyl phenyl ether	"	"
<i>m</i> -Cresyl methyl ether	"	"
<i>o</i> -Cresyl methyl ether	"	"
<i>p</i> -Cresyl methyl ether	"	"
$\beta\beta'$ -Dichloroisopropyl ether	"	"
$\beta\beta'$ -Dichloroethyl ether	"	"
$\gamma\gamma$ -Dichloroisopropyl ether	"	"
1-8 Epoxy <i>p</i> -menthane	"	"
Eugenol methyl ether	"	"
Resorcinol dimethyl ether	"	"

TABLE II

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS ALCOHOLS AT 20° C. IN ORDER OF DECREASING SOLUBILITY

Solvent	UO ₂ (NO ₃) ₂ · 6H ₂ O, gm. per 100 cc. of solvent	Th(NO ₃) ₄ · 4H ₂ O, gm. per 100 cc. of solvent
Dibutoxytetraethylene glycol	90	75.9
Isobutylcarbinol	57	30.0
Diethylcarbinol	57	9.1
<i>n</i> -Amyl alcohol	55	7.3
2-Ethyl butyl alcohol	49	9.0
Methyl amyl alcohol	43	—
<i>n</i> -Heptyl alcohol	43	—
Capryl alcohol	37	8.1
Geraniol	36	—
β,γ -Dibromopropyl alcohol	32	4.8
Undecanol	27	5.5
Tetradecanol	13	0.37

3. Addition of a ketone, aldehyde, or alcohol group enhances the solubility considerably.
4. For a given family the solubility decreases with increasing complexity of the molecule.

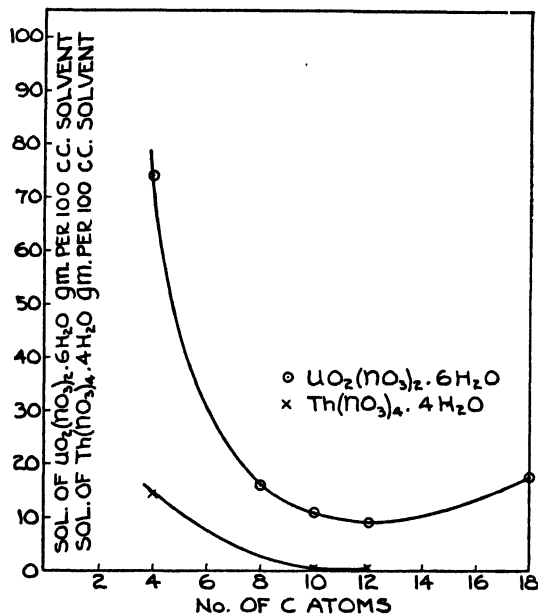


FIG. 1. Relation between solubility of uranyl nitrate hexahydrate and thorium nitrate tetrahydrate and number of C atoms in straight chain aliphatic ethers.

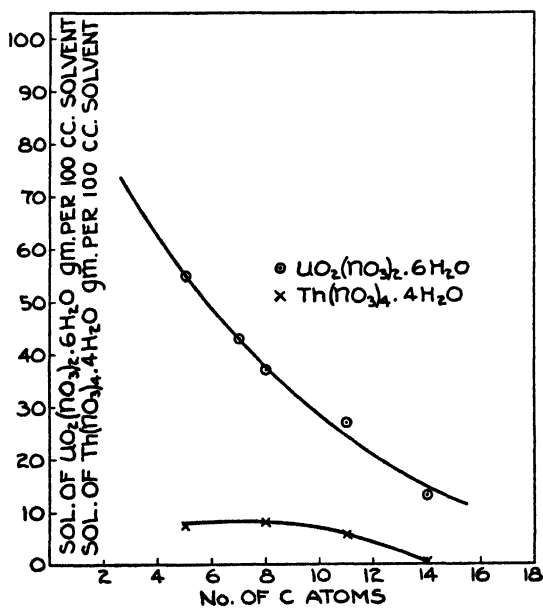


FIG. 2. Relation between solubility of uranyl nitrate hexahydrate and thorium nitrate tetrahydrate and number of C atoms in straight chain aliphatic alcohols.

TABLE III

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS ESTERS AT 20° C. IN ORDER OF DECREASING SOLUBILITY

Solvent	UO ₂ (NO ₃) ₂ · 6H ₂ O, gm. per 100 cc. of solvent	Th(NO ₃) ₄ · 4H ₂ O, gm. per 100 cc. of solvent
β-Ethoxyl ethyl acetate	125	—
Ethyl acetylglycollate	110	30.0
Ethyl acetate	82	—
Butylcellosolve acetate	77	—
Butyl acetate	68	6.5
Isopropyl acetate	64	20.0
sec-Butyl acetate	61	9.0
Amyl formate	56	30.0
n-Butyl propionate	55	27.5
Isoamyl acetate	55	18.0
Isobutyl acetate	50	16.0
Ethyl sebacate	48	—
Amyl acetate	46	9.2
Butyl adipate	40	—
n-Butyl sebacate	37	2.1
n-Amyl propionate	37	—
β-Phenyl ethyl acetate	35	—
Methyl phenyl acetate	33	—
Isobutyl propionate	31	—
Vinyl acetate	31	2.5
Isoamyl propionate	27	—
Amyl succinate	25	—
Amyl butyrate	25	4.3
Isoamyl formate	24	20.0
Amyl valerianate	21	4.2
Geraniol acetate	16	—
n-Butyl oxalate	9	0.03
Isoamyl n-caproate	7	2.4
Isoamyl oxalate	< 0.1	< 0.1
Benzyl n-butyrate	"	"
Butylcellosolve oleate	"	"
n-Butyl salicylate	"	"
Ethyl laureate	"	"
Ethyl myristate	"	"
Linalyl acetate	"	"
Phenyl ethyl benzoate	"	"
Isopropyl benzoate	"	"
n-Butyl nitrate	"	"
Diphenyl mono(<i>p</i> - <i>tert</i> -butylphenyl) phosphate	"	"
Di(<i>p</i> - <i>tert</i> -butylphenyl) monophenyl phosphate	"	"
Di(<i>o</i> -chlorophenyl) monophenyl phosphate	"	"

TABLE IV

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS KETONES AT 20° C. IN ORDER OF DECREASING SOLUBILITY

Solvent	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, gm. per 100 cc. solvent	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, gm. per 100 cc. solvent
Cyclohexanone	105	—
Methyl ethyl ketone + 15% xylene	100	75.0
Diethyl ketone	76	—
Methyl isobutyl ketone	75	26.0
Methyl <i>n</i> -amyl ketone	68	17.0
Diisopropyl ketone	41	6.6

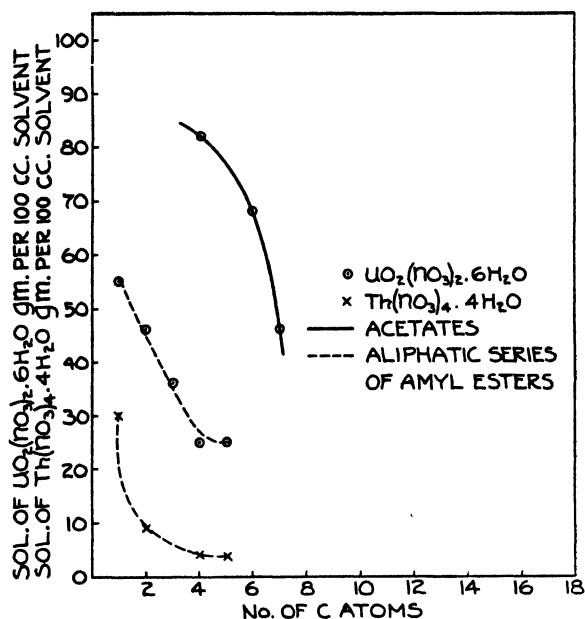


FIG. 3. Relation between solubility of uranyl nitrate hexahydrate and thorium nitrate tetrahydrate and number of C atoms in various aliphatic esters.

TABLE V

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS ALDEHYDES AT 20° C.

Solvent	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, gm. per 100 cc. solvent	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, gm. per 100 cc. solvent
Acetaldehyde	42	—
Citronellal	34	—
Anisaldehyde	27	—
<i>n</i> -Butyraldehyde	22	0.49

TABLE VI

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS HYDROCARBONS AT 20° C.

Solvent	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, gm. per 100 cc. solvent	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, gm. per 100 cc. solvent
α -Triisopropyltoluene	<0.1	<0.1
1-Pentene	"	"
Benzene	"	"
<i>p</i> -Isopropyltoluene	"	"
Linalool	"	"
Isopentane	"	"
Petroleum ether	"	"
Toluene	"	"
Turpentine	"	"
Xylene	"	"

TABLE VII

SOLUBILITIES OF URANYL NITRATE HEXAHYDRATE AND THORIUM NITRATE TETRAHYDRATE IN VARIOUS SUBSTITUTED HYDROCARBONS AT 20° C.

Solvent	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, gm. per 100 cc. solvent	$\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, gm. per 100 cc. solvent
Nitromethane	64	0.04
Triglycol dichloride	57	8.2
1-Nitropropane	8	—
2-Nitropropane	4	—
Nitrobenzene	1.5	—
Tetrabutylurea	6.0	6.0
Isoamyl bromide	< 0.1	<0.1
<i>m</i> -Chloroethylbenzene	"	"
α -Dichloro- α -diethylbenzene	"	"
Benzyl chloride	"	"
Carbon tetrachloride	"	"
1-Chloro-1-nitropropane	"	"
2-Chloro-2-nitropropane	"	"
1-Chloro-1-nitroethane	"	"
Chloroform	"	"
Dichlorobenzene	"	"
1,1-Dichloro-1-nitropropane	"	"
Ethylene bromide	"	"
Ethylene iodide	"	"
<i>s</i> -Tetrabromomethane	"	"
<i>s</i> -Tetrachlorethane	"	"
Trichlorethylene	"	"
Diethylamine	"	"
Diethylethylamine	"	"
Hydroxyethylethylenediamine	"	"
Triamylamine	"	"
Triethanolamine	"	"
Piperidine	"	"
Quinoline	"	"
β -Hydroxy- <i>o</i> -toluidine	"	"
2-Bromopyridine	"	"
Diamylphenol	"	"
2-Chloro-4,6-di- <i>tert</i> -amylphenol	"	"

Acknowledgments

The author wishes to acknowledge the assistance of J. Hebert and Miss C. E. Mackintosh in carrying out some of the analyses quoted above.

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THE COLORIMETRIC DETERMINATION OF SOME SYNTHETIC OESTROGENS¹

By R. A. DUNFORD

Abstract

The synthetic oestrogens, stilboestrol, hexoestrol, and dienoestrol give color reactions with nitric and nitrous acids, bromine, and certain phenol reagents, some of which can be adapted to their colorimetric determination. The use of Folin and Ciocalteu's phenol reagent is described for determination of the hormones in pharmaceutical products, using a Lumetron photoelectric colorimeter. The interference of other oestrogens and of phenolic preservatives and bactericides is considered and reference is made to a means of identifying the hormones by color reactions with antimony pentachloride in ethylene dichloride, and with an acetic-phosphoric acid reagent.

Introduction

The synthetic sex hormones, stilboestrol (I), hexoestrol (II), and dienoestrol (III) are all hydroxy derivatives of stilbene (IV) and vary only in the number of olefin linkages in the side chains. Hexoestrol is saturated, stilboestrol has one unsaturated linkage, and dienoestrol has a diene configuration (Fig. 1).

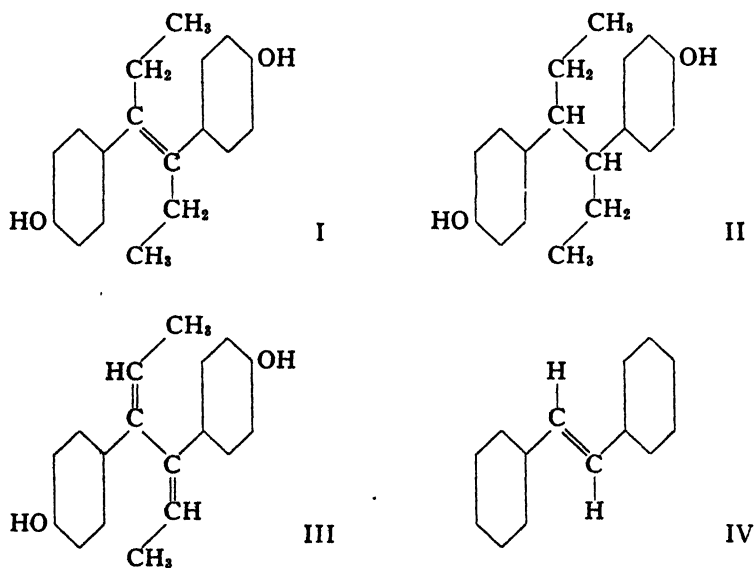


FIG. 1. Structural formulae of the hormones stilboestrol (I), hexoestrol (II) and dienoestrol (III), and of the parent compound stilbene (IV).

In the determination of these compounds in pharmaceutical products in which the dosage is of the order of from 0.1 to 5.0 mgm. a sensitive colorimetric procedure is required, and a number of methods of estimation have been suggested based either upon oxidation or bromination at the double bonds with

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formation of colored products or upon reaction of the phenolic groups with various phenol reagents.

Malpress's method (5) is based upon measurement of the orange color produced when a solution of the hormone in glacial acetic acid is treated with a small quantity of concentrated sulphuric and nitric acids and subsequently rendered alkaline with ammonia. This method has the disadvantage of low sensitivity—being unable to detect less than 0.5 mgm. of hormone, and is not specific, as many other organic compounds produce colors under these conditions.

Cocking (2) developed a color reaction for stilboestrol and dienoestrol based on bromination of the hormone in acetic acid solution and removal of excess bromine with phenol. This gives a green color on subsequent heating but it is suitable only as a qualitative test, for the shade as well as depth varies with concentration.

With a large excess of bromine a purple color is produced upon subsequent dilution with water; this color is apparently due to a colloidal compound, and it may be stabilized by gelatin. This reaction may be used as a basis for estimation of the pure hormones, but mere traces of fatty matter or stearates from oil solutions or tablets will inhibit the reaction.

Gottlieb's method (3, 4) depends upon the conversion of the oestrogen to the corresponding *o*-nitrosophenol by the action of nitrous acid, and the color measurement of the quinoid form in alkaline solution.

Experimental

The work in our laboratory upon the establishment of a standard method of estimation has been based upon the investigation of reaction of the hormones with the three commonly used phenol reagents, Gibbs's dibromoquinone-chloroimide reagent, Folin and Denis's reagent, and Folin and Ciocalteu's reagent.

It was found that Gibbs's reagent gave no color reaction with any of the three hormones; this bears out the theory that it does not react with *p*-substituted phenols. Folin and Denis's reagent is the molybdate-tungstate reagent specified for the assay of stilboestrol in the B.P. and U.S.P., while Folin and Ciocalteu's reagent is a modification of the above, containing lithium sulphate.

Both reagents are reduced by phenolic compounds, giving the molybdenum blue complex in alkaline solution. This complex has a rather flat spectral absorption curve, but measurements may best be carried out at 640 $m\mu$. Absorption curves plotted for the blue color, using 0.2 mgm. and 0.5 mgm. of stilboestrol, showed that the wave length giving maximum sensitivity was 640 $m\mu$.

The colors produced by the hormones with both Folin and Denis's, and Folin and Ciocalteu's reagent show conformance to Beers' law (Fig. 2) but a

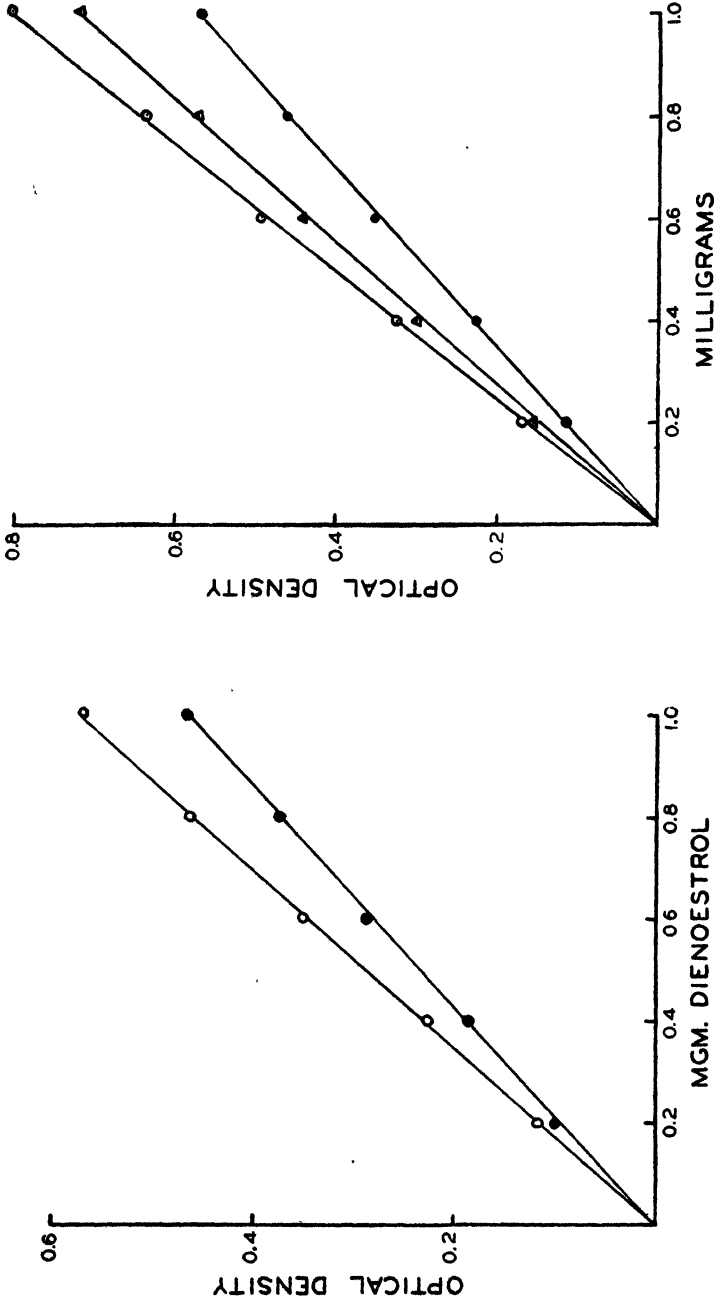


FIG. 2

FIG. 2. Calibration curves for dienoestrol using Folin and Denis's reagent (solid circles) and Folin and Ciocalteu's reagent (clear circles). Abscissae represent mgm. sample per 5 ml. of solution taken.

FIG. 3

FIG. 3. Calibration curves for hexoestrol (clear circles), stilboestrol (triangles), and dienoestrol (solid circles), using Folin and Ciocalteu's reagent. Abscissae represent mgm. sample per 5 ml. of solution taken.

steeper curve was given by Folin and Ciocalteu's reagent, indicating a somewhat greater sensitivity. Both reagents show a tendency to discolor upon storage, becoming dark green and unfit for use. Folin and Ciocalteu's reagent can, however, be readily regenerated by raising to boiling point, adding just sufficient bromine water dropwise to restore the full yellow color, boiling off any excess of bromine, and making up to its original volume on cooling. In view of this, Folin and Ciocalteu's was the reagent adopted for use, and standard curves were prepared for routine estimation of the three hormones on a Lumetron No. 402 EF photoelectric colorimeter, using filter M640.

Solutions of the hormones in 50% methanol (reagent grade) were prepared with concentrations ranging from 0.04 to 0.2 mgm. per ml., and 5 ml. portions of these solutions were pipetted into 100 ml. volumetric flasks. Five milliliters of the reagent was next added, and after standing for five minutes the solution was made alkaline by addition of 25 ml. of 10% sodium carbonate, well shaken, made up to 100 ml. with water, and allowed to stand for one hour for the color to develop. The solutions were centrifuged to remove the precipitate formed, and the clear liquid transferred to 13 mm. absorption cells. The percentage transmittance of each solution was measured, after setting the instrument for 100% transmittance on a blank prepared by treating 5 ml. of 50% methanol with the reagents in the same manner (Fig. 3).

The use of Folin and Ciocalteu's reagent has been applied to the determination of the hormones in tablets, ampoules, and ointment bases as follows.

Determination in Tablets

The uncoated tablets are crushed and a weighed quantity equivalent to about 5 mgm. of the oestrogen is extracted by maceration with ether.

Coated tablets should preferably have the color coat removed by agitating in a Gooch crucible with water until the dye coat is removed, and may then be extracted similarly to the uncoated tablets.

The ether extract is evaporated and the residue dissolved in 50 ml. of methanol and made up to 100 ml. with water. A 10 ml. portion is taken, the Folin and Ciocalteu's reagent added, made alkaline with 25 ml. of 10% sodium carbonate, and diluted to 100 ml. After standing one hour the solution is centrifuged, and its percentage transmittance measured in the colorimeter and compared to the standard curve.

Determination in Ampoules

Oil solutions of the hormones may be assayed by dilution of a measured volume with ether and extraction four times with *N*/1 sodium hydroxide. The combined alkaline extracts are acidified with dilute sulphuric acid and extracted five times with ether. The ether is then evaporated, the residue dissolved in alcohol, and the estimation carried out as for the tablets.

Determination in Ointment Bases

The oestrogens are sometimes compounded in ointment bases, or gynecological creams, and they may be estimated as for ampoules after first breaking down the emulsion by boiling under reflux with dilute hydrochloric acid and chloroform.

Five grams of the ointment or cream is dispersed in 25 ml. of water and 5 ml. of 5 *N* hydrochloric acid and 5 ml. of chloroform added. The mixture is refluxed for 20 min. or until a clear separation is obtained.

The chloroform layer is separated, and the aqueous layer washed with two further 10 ml. portions of chloroform. The bulk chloroform extracts are washed with two 5 ml. portions of water to remove traces of acid, and evaporated on a water bath. The residue is dissolved in ether and extracted with *N*/1 sodium hydroxide as for ampoules.

Results of some typical analyses of the above products are shown in Table I.

TABLE I

TYPICAL ANALYSES OF PHARMACEUTICAL PREPARATIONS OF SYNTHETIC OESTROGENS USING FOLIN AND CIOCALTEU'S PHENOL REAGENT

Preparation	Declared strength	Amount found, mgm.	Percentage found of declared amount
Dienoestrol tablets	0.3 mgm. per tablet	0.30	100
" "	0.3 " " "	0.29	96.5
" "	0.3 " " "	0.295	98
" "	1.0 " " "	0.96	96
" "	1.0 " " "	0.98	98
Stilboestrol "	1.0 " " "	0.97	97
" "	1.0 " " "	0.98	98
" "	1.0 " " "	0.96	96
" "	5.0 " " "	5.00	100
" "	5.0 " " "	4.90	98
Stilboestrol amps.	1.0 mgm. per cc.	0.98	98
" "	1.0 " " "	1.03	103
" "	5.0 " " "	5.10	102
Dienoestrol ointment	2.0 mgm. per fl. oz.	1.90	95
" "	5.0 " " "	4.85	97

Interference of Other Compounds

The reaction is not, of course, specific for the synthetic oestrogens, and is given by other phenolic compounds. Many of the preservatives for creams contain phenolic groups and a number have been investigated to determine their interference in the reaction.

It was found that while phenol and chlorocresol gave intense colors at low concentrations, the methyl and propyl *p*-hydroxy benzoates and phenylmercuric nitrate gave no color reaction in the concentrations in which they would be likely to be used as preservatives (Table II).

TABLE II

REACTION OF CERTAIN FUNGICIDES AND BACTERICIDES WITH FOLIN AND CIOCALTEU'S REAGENT

Compound	Concentration per 10 ml. sample, mgm.	Reaction	Per cent transmittance of solution
Chlorocresol	0.1	Positive	19
Phenol	0.1	Positive	15
Methyl- <i>p</i> -hydroxy benzoate	0.1	Negative	98
Propyl- <i>p</i> -hydroxy benzoate	0.1	Negative	98.5
Phenylmercuric nitrate	0.1	Negative	100.0
Stilboestrol (inserted for comparison)	0.02		66.0

Esters of the hormones, such as stilboestrol dipropionate, will not give a reaction unless they are first hydrolyzed, as they possess no free hydroxyl group. Similarly the natural oestrogen, oestradiol, gives a reaction, but its benzoic ester does not. The other natural sex hormones, progesterone and testosterone, are ketonic and give no color reaction.

Identification of the Hormones

The color reaction with Folin and Ciocalteu's reagent is given with hexoestrol, dienoestrol, and stilboestrol, and cannot be used to differentiate between them. Identification may be carried out by determination of the melting points of the separated hormones, which are:— stilboestrol, 170° C.; hexoestrol, 187° C.; dienoestrol, 233° C.

Two color reactions have also been published which can be used as a means of identification. Warren, Goulden, and Robinson (6) have found that solutions of stilboestrol and dienoestrol in ethylene dichloride will react with a 50% *V/V* solution of antimony pentachloride in the same solvent, to produce a red coloration. Hexoestrol gives no reaction other than a transient yellow tint. It should be noted that many other stilbene derivatives also give colors with this reagent.

A means of differentiating dienoestrol from the other oestrogens has been given by Boscott (1). The hormone, when dissolved in a few drops of glacial acetic acid and mixed with 1.8 ml. of 85% phosphoric acid, gives a sequence of colors from yellow to pink. On subsequent heating for one hour, adding 3 ml. of glacial acetic acid, and reheating, a purple coloration with a deep blue fluorescence is produced. Hexoestrol and dienoestrol do not give this reaction, but isodioestrol gives a similar color.

Acknowledgment

The author is indebted to the directors of The British Drug Houses (Canada) Ltd. for permission to publish these results.

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THE ALKALOIDS OF PAPAVERACEOUS PLANTS

XLII. *DENDROMECON RIGIDA* BENTH.¹

BY RICHARD H. F. MANSKE

Abstract

Aside from small uncrystallized residues the only alkaloids found in *Dendromecon rigida* Benth. are protopine and allocryptopine.

Since there appeared to be no record of the chemical examination of *Dendromecon rigida* Benth. it seemed important to determine the nature of the contained alkaloids. The plant is a shrub native to the southwestern coast of North America and is the only species generally recognized in the genus *Dendromecon* Benth.

While the quantity available was inadequate for a thorough study it can be stated that only two alkaloids, namely protopine and allocryptopine, are present in more than traces. A very small phenolic fraction yielded traces of a crystalline oxalate of doubtful purity.

Experimental

There was available one kilo of dried leaves and young shoots, which was ground and extracted with methanol in a Soxhlet apparatus. The solvent was removed from the extract and the residue digested with very dilute hydrochloric acid. After cooling, the pale yellow aqueous solution was decanted from the resinous material through a layer of charcoal. The clear filtrate was extracted with chloroform until the extract was colorless. Examination of the chloroform yielded only a trace of protopine.

Protopine

The aqueous solution which had been extracted with chloroform was basified with ammonia and again extracted with chloroform. The residue from the chloroform extract was dissolved in dilute hydrochloric acid, and the solution filtered with the aid of charcoal, and treated with an excess of sodium hydroxide. The precipitated base was filtered off, washed, and dried. (When the alkaline filtrate was saturated with carbon dioxide and exhausted with ether it yielded a trace of protopine and a small amount of an amorphous base which afforded a quantity of a crystalline oxalate insufficient for further examination.) The dried base was dissolved in hot methanol, filtered, and evaporated to a small volume. Seeding with a crystal of protopine yielded an immediate crop of protopine weighing 0.6 gm. After one recryst-

¹ Manuscript received February 26, 1949.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada, and from the Research Laboratories, Dominion Rubber Co. Ltd., Guelph, Ontario. Issued as N.R.C. No. 1973.

tallization from chloroform-methanol it melted sharply at $210^{\circ}\text{C}.$ * either alone or in admixture with an authentic specimen of protopine.

Allocryptopine

The methanolic filtrate from the protopine was concentrated to a thin syrup and seeded with a crystal of allocryptopine. The base, which crystallized immediately (0.2 gm.), was recrystallized from hot methanol; it then melted at $160^{\circ}\text{C}.$ either alone or in admixture with authentic allocryptopine.

The final mother liquor from the above alkaloids on further examination yielded only small amounts of the above two alkaloids.

* *Melting points are corrected.*

DINITRATION AND DEALKYLATION OF *p*-CYMENE¹

By O. C. W. ALLENBY² AND R. V. V. NICHOLLS

Abstract

An investigation of the dinitration of *p*-cymene (4-isopropyltoluene) has been carried out, with particular regard to determining the effects of varying the temperature, the nitric acid, sulphuric acid, and water contents of the system, the rate of addition of *p*-cymene, and the stirring time upon the yields of 2,6-dinitrocymene and 2,4-dinitrotoluene. Optimum nitrating conditions have been determined and the relative constancy of the dinitrocymene : dinitrotoluene ratio over a wide range of conditions has been established. Yields of the order of 55% dinitrocymene and 25% dinitrotoluene have been obtained. Various theories are offered with a view to explaining some of the more important observations.

Introduction

The action of nitrating mixtures on *p*-cymene (1-methyl-4-isopropylbenzene) has been fairly extensively investigated by a number of workers. Mono-, di-, and tri-nitrated products can be obtained by varying the reaction conditions. Attempts at mononitration have involved the addition of nitric acid to cymene (4, 10, 11, 19), addition of cymene to mixed nitric and sulphuric acids (31, 32), and addition of "mixed acid" to a mixture of cymene, sulphuric acid, and acetic acid (15, 21, 16, 28). The last method has been perfected by Doumani and Kobe (8) and results in consistent yields of 86 to 90% 2-nitrocymene and 8 to 10% 4-nitrotoluene (by loss of the isopropyl group). Wide variations in nitric acid, sulphuric acid, and acetic acid content, time of addition, and presence of emulsifying agents do not alter these values appreciably.

Dinitration of cymene has been achieved by the addition of cymene to nitric acid (3, 12, 31), and by the addition of cymene to mixed acid (1, 3, 15, 17, 18, 29, 31, 32). To Alfthan (1) goes the credit for the conclusive identification of the products, which were shown to be principally 2,6-dinitrocymene and 2,4-dinitrotoluene. He also devised a method for separating them by recrystallization from ethanol. From none of this work is it possible to draw accurate conclusions concerning the yields of the two principal products or the effect of reaction variables on these yields.

Trinitration of *p*-cymene has been accomplished with difficulty, by prolonged treatment of *p*-cymene, or 2,6-dinitrocymene, either with a mixture of fuming nitric acid and concentrated sulphuric acid (9, 12), or with a mixture of fuming nitric acid and oleum (13). The principal product was probably 2,3,6-trinitrocymene and was obtained probably in low yield.

The removal of alkyl groups attached to aromatic nuclei (dealkylation) under nitrating conditions has been repeatedly observed by a number of

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workers (Claus (7), Qvist (24), Smith *et al.* (25, 26, 27, 28)). The removal of an isopropyl group during the nitration of a *p*-cymene derivative (*p*-cymene-*o*-sulphonic acid) was first observed by Hintikka (14). The same process was probably responsible for the appearance of a toluene derivative on the nitration of 2-chlorocymene as observed by Lubs and Young (20). Doumani and Kobe (8) have given detailed consideration to dealkylation as it accompanies mononitration of *p*-cymene. The loss of an isopropyl group was also observed by Alfthan (1) during the dinitration of *p*-cymene, and by Halse and Dedichen (13) during the trinitration of cymene.

Several workers have speculated about the nature of the dealkylation process. Claus and Qvist (7, 24) have suggested that the first step is oxidation of the alkyl group to a carboxyl group by nitric acid, followed by substitution of the carboxyl group by a nitro group. Smith *et al.* (25, 26, 27, 28) have postulated that methylbenzenes are first converted to benzyl nitrates by nitric acid, and these in turn to nitro compounds by sulphuric acid. Doumani and Kobe (8) have criticized these views, stating that oxidation plays no part in the process, for if the *p*-cymene is properly emulsified during nitration no oxides of nitrogen are formed. Rather they suggest that the *p*-cymene is cleaved directly by the nitric acid, the tolyl group appearing as a nitrotoluene and the isopropyl group as propanol-2. They were able to isolate propanol-2 from the spent mixed acid, though admittedly not in quantitative yields.

The present investigation was undertaken to determine optimum conditions for the preparation of 2,6-dinitrocymene and 2,4-dinitrotoluene and to devise improved methods for the separation of these compounds.

Experimental Section

Purification of p-Cymene

Sulphite turpentine (secured from the Brown Corporation, Berlin, N.H.) had been purified by steam distillation from sodium hydroxide solution, and was subsequently treated with cold 95% sulphuric acid until the acid was no longer colored, washed with dilute sodium bicarbonate solution, dried over calcium chloride, and distilled through a five-plate column. *p*-Cymene, having the following physical constants, boiling range (corr.) 176.8° to 177.3° C., n_D^{20} 1.4906 to 1.4909, was used in all the runs reported below. By actual experiment it was found that a less pure grade of *p*-cymene, obtained by washing with alkali followed by steam distillation, give substantially the same results on nitration. In agreement with Mann *et al.* (21) it has been found that refluxing over sodium metal does not yield a purer product.

Standard Conditions of Nitration

A convenient nitration vessel was found to be a 500 cc., three-necked, round-bottomed Pyrex flask, equipped with standard taper ground glass joints and surrounded by a cooling bath adjusted to a temperature about 5° C. below the designated reaction temperature. The flask was equipped with a

separatory funnel and carbon dioxide inlet tube, an efficient stirrer with plain bearing, and a thermometer with bulb immersed in the reaction mixture. All nitrations were carried out under carbon dioxide and with very rapid stirring. The separatory funnel was calibrated and its outlet tube drawn down to a fine jet to assist in obtaining a uniform rate of delivery.

A solution of 60 gm. (0.915 mole) 96% nitric acid and 120 gm. (1.175 moles) 96% sulphuric acid was placed in the nitration vessel and the temperature adjusted to 30° C. by external cooling. To this was added 30 gm. (0.224 mole) *p*-cymene with vigorous stirring over a period of two hours \pm 10 min. Stirring was continued for an additional hour. Throughout the addition and stirring periods the temperature of the reaction mixture was maintained to within one degree of that desired. The reaction mixture was then poured onto ice.

The water layer was separated and extracted repeatedly with benzene; the washings were then combined with the nitration product proper. The benzene solution was washed several times with water containing a little salt and with 10% sodium carbonate solution. Separation of the benzene layer was greatly assisted by filtering to remove a small quantity of suspended solid material. The organic layer was then dried over anhydrous sodium sulphate, and the benzene removed at reduced pressure (100 mm.).

Identification of the Nitration Products

A partial separation of the nitration product into its components was achieved by fractional distillation under reduced pressure. Because of the highly viscous nature of the material and the close similarity of the boiling point curves of 2,4-dinitrotoluene and 2,6-dinitrocymene, it was impossible to do more than separate the mono from the dinitro derivatives. Fractionation was carried out in a $\frac{1}{2}$ by 12 in. jacketed column loosely packed with three-turn $\frac{3}{8}$ in. diam. helices. Unreacted *p*-cymene was taken off as a forerun at 100 mm. pressure, the distillation proper being carried out at 2.5 to 4.0 mm. The first fraction (generally small) consisted mainly of 2-nitrocymene and a little 4-nitrotoluene. Fraction II contained the 2,6-dinitrocymene and 2,4-dinitrotoluene. High boiling residue left in the still pot was small in amount.

The determination of the proportions of 2,4-dinitrotoluene and 2,6-dinitrocymene in Fraction II was accomplished by measuring the refractive index at $40 \pm 0.2^\circ$ C. The composition could then be determined from Table I.

An investigation into the possibility of separating 2,6-dinitrocymene from 2,4-dinitrotoluene in Fraction II by fractional crystallization was also undertaken. Alfthan (1) had suggested ethanol and Kyker and Bost (18) had suggested methanol as suitable solvents. These were not found to be satisfactory. However, good results were obtained with Skelly Solve B (b.p. 60° to 68° C.). Fraction II was shaken with three times its weight of this solvent at room temperature. After settling, the solvent was decanted and cooled to 0° C. The oil that separated was removed and the supernatant

liquid again cooled to -60°C . (or the solvent simply evaporated off). The solid that separated was very rich in 2,6-dinitrocymene. By actual test 2,6-dinitrocymene containing 30% dinitrotoluene by weight after such a

TABLE I
REFRACTIVE INDEX - COMPOSITION VALUES FOR
VARIOUS DINITROTOLUENE-DINITROCYMENE
MIXTURES

Per cent dinitrotoluene by weight	n_D^{40}
0	1 5368
8 97	1 5400
17 20	1 5428
22 75	1 5447
28 10	1 5468
35 15	1 5491
50 00	1 5543
60 35	1 5580
M.p. dinitrocymene	53° to 54°C .
M p. dinitrotoluene	71° to 72°C .

treatment gave an oil in 13% yield from the first crystallization at 0°C . and a solid in 23% yield from the second stage. The oil contained 19% dinitrotoluene and the solid 6% dinitrotoluene. Substantially pure 2,6-dinitrocymene was obtained by seeding an alcohol solution of this solid. By a repetition of this process the entire nitration product could be separated. This method of purification proved to be too time consuming, however, to be used as routine method of analysis for the large number of runs involved.

Experimental Results

Each of the various variables (temperature, nitric acid concentration, sulphuric acid concentration, etc.) was investigated over a suitable range,

TABLE II
EFFECT OF VARIATION OF TEMPERATURE

Run No.	Temp., $^{\circ}\text{C}$.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture, %	Yield, %	
		Mononitro	Dinitro			D.N.C.	D.N.T.
1 & 2*	-20	—	37.3	4 7	28 2	53 3	25.9
3	- 6	—	38.8	5 0	27 5	56 0	26.1
4	6	0.1	39.0	2 6	27.0	56 6	25.8
5	16	—	37.9	3 9	27 0	55.2	25.1
6 & 7*	30	1.1	34 6	5.0	27.1	50.3	23.0
8	40	2.2	30.3	5.3	27.7	43 6	20.6
9	60	1.6	21.5	6.0	33.4	28.5	17.6

* Average of two runs.

the remaining variables being maintained at the values indicated under "standard nitrating conditions". The results obtained have been summarized in Tables II to VII with an accompanying graph in the case of Table IV.

TABLE III

EFFECT OF VARIATION OF NITRIC ACID CONTENT OF MIXED ACIDS

Run No.	96% HNO ₃ , gm.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture, %	Yield, %	
		Mononitro	Dinitro			D.N.C.	D.N.T.
25*	24.5	0.3	13.0	4.0	28.5	18.5	9.1
26	41.2	2.3	24.2	3.0	27.8	34.8	16.5
28	48.7	3.4	28.6	3.7	27.5	41.3	19.3
6	60.0	1.1	34.6	5.0	27.1	50.3	23.0
31	67.5	0.2	35.3	5.0	26.2	51.9	22.7
32	70.0	—	37.0	4.9	26.5	54.2	24.1
33	100.0	0.1	37.8	4.3	28.2	54.0	26.2

* Difficult to prevent "fume-off". Considerable quantities (15 gm.) of unchanged *p*-cymene recovered.

TABLE IV

EFFECT OF VARIATION OF SULPHURIC ACID CONTENT OF MIXED ACIDS

Run No.	96% H ₂ SO ₄ , gm.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture, %	Yield, %	
		Mononitro	Dinitro			D.N.C.	D.N.T.
17*	0	7.9	9.7	5.6	32.7	12.9	7.8
18	40	8.5	18.0	5.5	29.5	25.3	13.0
19	70	7.1	25.9	5.4	28.6	36.8	18.2
20	100	4.3	31.2	4.3	27.7	44.9	21.2
6	120	1.1	34.6	5.0	27.1	50.3	23.0
22	150	0.3	36.6	4.1	27.7	52.7	24.9
23	200	0.3	37.1	4.1	27.6	53.5	25.1

* In this run, 2.9 gm. of unchanged cymene recovered.

TABLE V

EFFECT OF VARIATION OF ADDITION TIME

Run No.	Addition time, hr.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture, %	Yield, %	
		Mononitro	Dinitro			D.N.C.	D.N.T.
38	1/3	—	38.5	3.6	25.8	56.8	24.3
39	1	0.1	37.7	3.5	26.3	55.3	24.3
41	2	1.2	35.9	4.1	26.7	52.4	23.4
42	5	2.1	33.4	4.1	27.6	48.2	22.6
43	8	2.6	31.0	5.3	29.5	43.5	22.4
44	11	2.1	30.0	5.6	29.4	42.2	21.6

In all cases "Weight of products" excludes unreacted *p*-cymene, if any, and alkali-soluble or alkali- and benzene-insoluble products, if any. "Residues" means the weight of nondistillable material. "D.N.T. in mixture" means

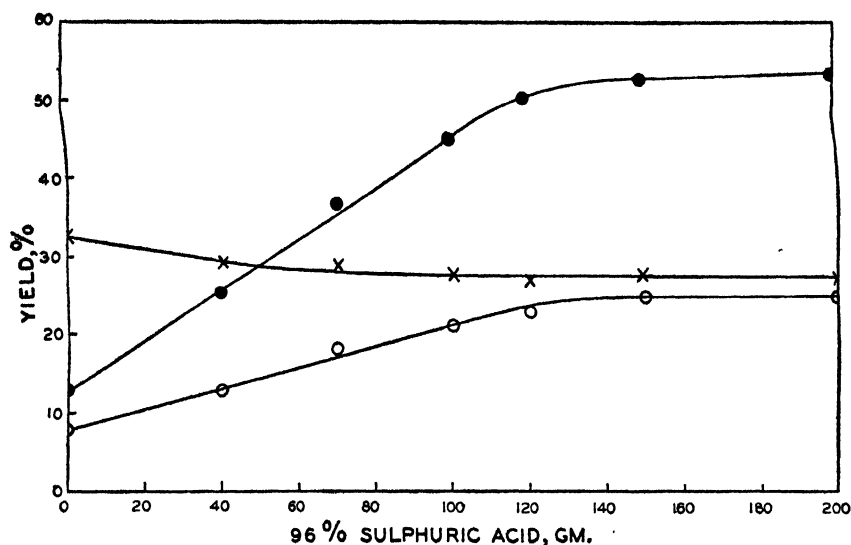


FIG. 1. Effect of variation of sulphuric acid content on nitration of *p*-cymene.

- Yield of dinitrocymene.
- Yield of dinitrotoluene.
- × Per cent dinitrotoluene in mixture.

TABLE VI

EFFECT OF VARIATION OF STIRRING TIME AFTER COMPLETE ADDITION OF CYMENE

Run No.	Stirring time, hr.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture %	Yield, %	
		Mononitro	Dinitro			D.N.C.	D.N.T.
34	1/2	1.4	33.9	4.4	26.6	49.6	22.2
35	1	1.1	34.6	4.3	27.1	50.2	23.0
36	2	1.2	35.9	4.2	26.4	50.8	22.5
37	3	0.8	35.6	—	26.7	52.0	23.4

the per cent dinitrotoluene in the dinitration fraction. "Yields of dinitrocymene and dinitrotoluene" were calculated on the total amount of *p*-cymene used; no allowance was made for *p*-cymene recovered.

With the object of comparing the relative ease of the nitration of cymene with the nitration of other simple aromatic compounds, the mononitration of cymene was attempted by means of a typical procedure employed in the mononitration of benzene. A nitrating mixture consisting of 25.5 gm. 96% sulphuric acid and 20.1 gm. 70% nitric acid was added dropwise over a period of 70 min. to 30 gm. of cymene at 30° C. with vigorous stirring. The mixture was then heated to 56° C. and maintained at this temperature for 50 min.,

TABLE VII
MISCELLANEOUS VARIATIONS IN NITRATING CONDITIONS

Run No.	Weight of products, gm.		Residues, gm.	D.N.T. in mixture, %.	Yield, %	
	Mononitro	Dinitro			D.N.C.	D.N.T.
46	1.5	35.3	3.9	27.2	51.0	23.5
47	1.4	34.8	4.4	27.0	50.6	23.0
48	1.6	34.1	5.0	27.2	49.5	22.8
51	1.2	35.5	4.7	27.7	51.1	24.2
54	—	2.3	3.3	20.4	3.6	1.2
55	—	20.5	9.9	29.4	28.9	14.8
59	11.7	11.9	2.7	25.5	19.0	7.7
60	0.8	27.4	3.7	19.0	59.0	17.1
64	—	38.7	3.8	26.8	56.4	25.4

NOTES:

- Run 46* Standard nitrating conditions. Small amount of cobalt nitrate present.
Run 47 Standard nitrating conditions. Small amount of zinc nitrate present.
Run 48 Standard nitrating conditions. Small amount of nickel nitrate present.
Run 51 Standard nitrating conditions. Nitric acid decolorized with urea nitrate.
Run 54 Standard nitrating conditions. Nitric acid added to cymene in sulphuric acid.
Run 55 Standard nitrating conditions. Mixed acids added to cymene.
Run 59 Nitration of 2-nitrocymene under conditions employed in adding second nitro group to mononitrotoluene (see text).
Run 60 Nitration of mononitrocymene under standard nitrating conditions using one-half the mixed acid normally employed.
Run 64 Nitration done under optimum conditions for all variables (see Discussion of Results).

with continuous stirring. The now nearly black solution was poured onto ice and worked up in the usual manner. A forerun of 13.6 gm. of unchanged cymene was followed by 5.3 gm. of yellow product boiling over a wide range (65° to 122° C. at 14.8 mm.) though the main fraction came off at temperatures corresponding to mononitrated material. A considerable amount of residue (9.3 gm.) remained in the pot.

The ease of addition of a second nitro group to mononitrocymene under conditions that are known to operate successfully in a similar nitration stage in the production of T.N.T. was also determined. To an acid mixture composed of 15.6 gm. of 96% nitric acid, 42.4 gm. 96% sulphuric acid, and 4.95 gm. of water at 85° C., 30 gm. of mononitrocymene ($n_D^{20} = 1.4291$) was added over a 20 min. period with stirring. After being held at 92° C. for 10 min., the mixture was allowed to stand for a similar length of time before pouring on ice. The results are tabulated in Table VII, Run 59.

Discussion of Results

Effect of Temperature (Table II)

Maximum yields of dinitrocymene and dinitrotoluene were obtained at approximately 6° C. This is in contradiction to the results of Kyker and Bost (18), who reported that the absolute yields steadily increase with fall

in temperature. Production of nitrogen oxide fumes during nitration increased with rising temperature until at 60° C. oxidation was so violent that mixtures tended to fume off. The color of the undistilled products also became progressively darker (they were almost black at 60° C.). The quantity of alkali-soluble materials produced during nitration increased in the same way, a very marked rise taking place at 60° C. Hence, lowered yields at higher temperatures are probably due to the occurrence of oxidation and sulphonation as side reactions.

Quantities of alkali- and benzene-insoluble material were produced in increasing amounts as the temperature was reduced below 30° C. The nature of this product was not determined, but its appearance probably accounts for the drop in yield of nitrated products at temperatures below the optimum.

Effect of Nitric Acid Content of the Nitrating Mixture (Table III)

The effect of variations in the nitric acid content of the nitrating mixture upon the ratio of the dinitrotoluene to dinitrocymene in the products appears to be negligible. (There is a suggestion of a minimum at 70 to 75 gm. nitric acid for 30 gm. *p*-cymene). When the quantity of nitric acid was below 70 gm., the yield of dinitrocymene and dinitrotoluene dropped rapidly, however. Under these conditions oxidation was extensive, large volumes of nitrogen oxide fumes were produced and the quantity of alkali-soluble products formed increased rapidly. Considerable amounts of cymene were also recovered unchanged. The yield of dinitrated products remained substantially unaltered when the nitric acid used was increased beyond 70 gm. This is the amount required assuming quantitative dinitration of the cymene and allowing sufficient acid to convert the isopropyl groups removed (as the result of dinitrotoluene formation) into isopropyl nitrate.

Effect of Sulphuric Acid Content of the Nitrating Mixture (Table IV)

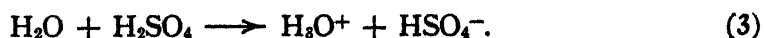
It has been shown by Bennett *et al.* (5) that the vigorous nitrating action of mixed acids is due to the presence of the active nitronium ion, NO_2^+ , formed by the reaction:



Nitration of an aromatic compound is stated to be due to simultaneous attack on the aromatic nucleus by the nitronium ion and a proton acceptor such as HSO_4^- :



In such acid mixtures sulphuric acid is immobilized by an amount equivalent to the water present since there is no doubt that water reacts in an excess of sulphuric acid completely according to the equation:



Hence it is only the sulphuric acid in molar excess of this water that is effective in the production of the active nitrating agent by Equation (1). Nitration requires not only the attachment of a cation to the benzene nucleus, however,

but also the removal of a proton. The most obvious proton acceptor in a water-sulphuric acid medium is the bisulphate ion, and its concentration is increased with increase in water content. Increase in the water content, however, reduces the concentration of NO_2^+ ion, hence optimum nitrating condition will be a compromise between these two opposing factors. Bennett *et al.* (6) have shown that 92% sulphuric acid is the medium in which the velocity of nitration of 2,4-dinitrotoluene is a maximum. Martinsen (22) found that the velocity of nitration of a number of substituted benzenes was greatest in 90% sulphuric acid. Hence the most favorable concentration appears to be approximately 90 to 92%.

Using 30 gm. (0.224 mole) cymene and 60 gm. (0.915 mole) 96% nitric acid, experimental results obtained in this investigation have shown that the yield of both dinitration products increases with the amount of sulphuric acid present, reaching a maximum at approximately 130 gm. The water content of a typical run carried out with this amount of acid was determined at the beginning and end of the nitration with the Karl Fisher reagent. A mean of these two figures can be taken as the average water content of the system during the reaction. The value obtained, 93%, is comparable with Bennett's figure of 92%. Beyond this point, further amounts of sulphuric acid do not appear to have any marked influence, as can be seen by Fig. 1.

The ratio of dinitrotoluene to dinitrocymene remained practically constant at about 27.5% when the sulphuric acid content of the nitrating mixture was 100 gm. or more for 30 gm. *p*-cymene. When the amount of acid was decreased below this amount a slight rise in this ratio occurred. Increased oxidation was observed at the lower sulphuric acid contents. Preferential attack on the isopropyl group in the cymene during this side reaction could account for such a rise in the dinitrotoluene-dinitrocymene ratio.

Effect of Variation of Addition Time (Table V)

Over-all yields of dinitrated products dropped gradually with increase in the addition time of the cymene to the nitrating mixture. A corresponding increase in the quantity of oxidation products occurred; this probably accounts for lowered yields and for a rise in the dinitrotoluene-dinitrocymene ratio.

Effect of Variation of Stirring Time (Table VI)

This variable does not appear to have an appreciable effect on the products obtained.

Miscellaneous Variations in Nitrating Conditions (Table VII)

Very poor results were obtained when the mode of addition of the reactants was other than that stipulated under "standard nitrating conditions". In Run 54, the nitric acid was added dropwise to the mixture of cymene and sulphuric acid. Considerably more heat was evolved than in a normal run and the mixture had a great tendency to fume off. Since the amount of dinitrated material was extremely small, the value for "D.N.T. in mixture" (20.4%) means little. In Run 55, the combined mixed acids were added to

the cymene, with results similar to those of Run 54 though yields were higher. The behavior of cymene in this respect is in contrast with that of other aromatics such as benzene and toluene.

The addition of various metallic nitrates (Runs 46, 47, 48) appeared to have no appreciable effect on the results. Phillips (23) reported that in the sulphonation of cymene, the addition of small quantities of such metallic salts also had little effect.

It will be observed that on mononitrating 2-nitrocymene by the "standard conditions" (making suitable corrections in the quantities of nitrating mixture employed—Run 60), the amount of dinitrotoluene produced dropped from the normal 27% to a value of 19%. The difference in these percentages (i.e., 8%) is the value for the amount of *p*-nitrotoluene produced in the mononitration of cymene as found by Kobe and Doumani (15). It would thus appear that dinitration of cymene proceeds in two stages. In the mononitration stage the per cent cleavage of the isopropyl group is 8%; in the next stage a further 19% is removed. The greater cleavage that occurs in the second stage would be anticipated since the nitro group is *meta* directing—hence it aids removal of the isopropyl group which in 2-nitrocymene is *meta* to it.

From an analysis of the various tables it is possible to select conditions that should give maximum yields of products. These conditions are as follows (for a 30 gm. sample of cymene): 96% nitric acid, 75 gm.; 96% sulphuric acid, 150 gm.; temperature, about 0° C.; addition time, as short as possible; stirring time, not critical but conveniently one hour. The results of a nitration carried out under these conditions will be found in Table VII—Run 64 (an addition time of 15 min. being used.) The yields were not appreciably better than those obtained under the conditions of optimum addition time alone (Table V—Run 38). It would appear, then, that there is but little possibility of increasing these values beyond this point.

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FURTHER DEVELOPMENTS IN THE VISTEX METHOD FOR THE DETERMINATION OF THE INTRINSIC VISCOSITY OF HIGH POLYMERS¹

BY D. A. HENDERSON AND N. R. LEGGE

Abstract

The intrinsic "vistex" viscosities of several series of butadiene-styrene copolymers of varying conversion and average molecular weight, dissolved directly from the latex in the vistex solvent mixture (toluene-isopropanol, 80/20 by volume), have been investigated and compared with the intrinsic viscosities of the corresponding coagulated, dried polymers dissolved in toluene. The intrinsic viscosity in toluene, $[\eta]_T$, is related to the intrinsic vistex viscosity, $[\eta]_V$, in toluene-isopropanol by the equation:—

$$\log[\eta]_T = 0.0827 + 1.08 \log [\eta]_V.$$

Hence, viscosity average molecular weight may be calculated from vistex measurements.

A further development of the method has shown that, once the latex is dissolved in the vistex solvent, the solution may be diluted, within certain defined limits, by the addition of pure solvent (toluene) to obtain the several levels of concentration of polymer required for the determination of intrinsic viscosity. It is then possible, by extrapolation to zero concentration of polymer, to obtain a value for the intrinsic viscosity that is equal to the conventional intrinsic viscosity of the polymer in pure solvent after coagulation and drying under very mild conditions. The viscosity characteristics of butadiene-styrene copolymers of varying conversion appear to be represented, at conversions below the gel point, by the equation

$$\frac{\ln \eta_r}{c} = [\eta] - \beta'[\eta]^nC,$$

where β' and n are constants of the order of 0.25 and 1 for solutions in toluene and 0.1 and 2.5 respectively for vistex solutions. Distinct changes in β and/or n have been found at conversions in the region of and beyond the gel point.

Introduction

The term vistex was first used by Baker *et al.* (5) in 1943 to describe measurements of the dilute solution viscosity of polymer dissolved directly from the latex in a mixture of hydrophobic and hydrophilic solvents such as xylene and pyridine. Thus, the introduction of further unknown variables by coagulation and drying was avoided and a more direct evaluation of polymerization variables could be obtained. The method was primarily developed to follow changes in polymer characteristics with conversion during the production of GR-S.

The type and amount of hydrophilic solvent required to bring the water into solution was found to be fairly critical. In agreement with the results

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Contribution from the Physical Research Laboratory, Research and Development Division, Polymer Corporation, Sarnia, Ont.

with other systems (1) it was found that the addition of the hydrophilic non-solvent lowered the inherent viscosity* of the polymer. A number of solvent systems were tried and preference was given to systems in which the highest relative viscosity was obtained, on the grounds that the most highly extended chains would give the highest viscosity increment per unit chain length. The solvent system chosen was xylene-pyridine (75/25) which was found to give clear solutions of 1 ml. of GR-S latex per 100 ml. of solution at 40° C. Viscosity measurements had to be made at that temperature.

It was known that the inherent viscosity of the polymer increased at higher conversions and Baker *et al.* (5) postulated that there should be a maximum in the inherent vistex viscosity vs. conversion relation if measurements are made up to and beyond the gel point. Although the presence of microgel of high swelling volume may raise the inherent viscosity somewhat, as the density of cross linkages increases this contribution of dispersed microgel particles to the inherent viscosity will decrease and the inherent viscosity will drop. This maximum in the curve was found (5, 6, 14) to occur at the same conversion for both vistex and intrinsic viscosity data.

Later, Kolthoff (15) proposed the use of benzene-isopropanol (80/20) as a vistex solvent. This system dissolved the latex immediately without heating and permitted the determination of viscosity at room temperature. Inherent viscosities obtained with this system were somewhat lower than those determined in the xylene-pyridine system but gave relatively the same information. The addition of aqueous alkali or soap to the vistex system caused a reduction in the inherent viscosity that was due only to the amount of water added. Generally, nonsolvent was found to lower the inherent viscosities of polymers of high molecular weight much more than those of polymers of low molecular weight. Harris and Kolthoff (12) correlated values obtained by the vistex method (benzene-isopropanol) with inherent viscosities in benzene for a number of GR-S type polymers. The inherent viscosity in benzene, $\{\eta\}_B$, was found to be related to the inherent vistex viscosity, $\{\eta\}_{BIW}$, by the following equation:—

$$\{\eta\}_B = A \cdot \{\eta\}_{BIW},$$

where A varies from 1.16 at $\{\eta\}_{BIW} \simeq 0.3$ to 1.42 at $\{\eta\}_{BIW} \simeq 1.8$. It was emphasized that the table of correlated data was valid only if 1 gm. of partially vented latex was used per 100 ml. of solution.

* Terminology used is in accordance with that proposed by Cragg (7) except that we have introduced the word "vistex" into the appropriate terms when the vistex method was used, i.e., the polymer dissolved directly from the latex. Brief definitions are given below:—

ν_{solution} = kinematic viscosity of the polymer solution,

ν_{solvent} = kinematic viscosity of the solvent,

$$\nu_r = \frac{\nu_{\text{solution}}}{\nu_{\text{solvent}}},$$

$$\frac{\ln \nu_r}{c} = \text{inherent kinematic viscosity},$$

$$\lim_{c \rightarrow 0} \frac{\ln \nu_r}{c} = [\nu] = \text{intrinsic kinematic viscosity}.$$

It was noted in reviewing all the previous work that inherent viscosity, $\frac{\ln \eta_r}{c}$, rather than its limiting value, the intrinsic viscosity, $\lim_{c \rightarrow 0} \frac{\ln \eta_r}{c}$, was determined. This is common practice in rapid, routine determinations. However, these one-point determinations and also those suggested by Cragg *et al.* (9) have been found inadequate to represent the viscosity characteristics of the wide ranges of polymers studied in our laboratories. Moreover, there did not appear to be available any suitable method of calculation of the intrinsic viscosity of the polymer in a good solvent and hence the viscosity average molecular weight, from the corresponding intrinsic viscosity. Therefore, a further study of the viscometer method was commenced. The solvent system chosen was toluene-isopropanol (80/20) and limiting, intrinsic values were determined throughout the investigation. Intrinsic viscosities of several series of butadiene-styrene copolymers of varying average molecular weight and conversion have been determined and correlated with the intrinsic viscosities of the coagulated, dried polymer in toluene and also in the viscometer solvent.

Experimental Procedure

Viscometer Viscosity Procedure

The latex, about 1 ml., was added to about 100 ml. of the solvent mixture and dissolved readily after a few minutes agitation. The latex can be weighed precisely and the concentration calculated from its solids content. However, it was frequently found advisable to filter the solution through a sintered glass filter, porosity C, and this often caused a change in concentration. The concentration of the solution was determined by evaporating 20 ml. on a steam plate for about 15 min. after the solvent had disappeared. The concentration value was corrected for nonpolymer content and expressed in grams of polymer per 100 ml. of solution.

The solutions were brought to $30.4 \pm 0.03^\circ \text{C.}$ by suspending the flask in the bath for at least 10 min. The flow times were measured in an Ubbelohde viscometer modified by the installation of a large bulb to allow dilution of the solution while in the viscometer.

The viscometer had the following characteristics:—

L , length of capillary	8.97 cm.
R , radius of capillary (precision bore)	0.254 cm.
H , mean hydrostatic head (head at $t/2$ sec.)	12.12 cm.
t_0 , time of efflux at 30.4°C. for toluene	105.0 sec.
for toluene-isopropanol (80/20)	112.2 sec.
V , volume of efflux	= 4.03 ml.
Lt_0/V for toluene	= 233.8
τ , mean shearing stress at the wall ($Hdg R/2L$)	= 14.4

Kinetic energy corrections were determined with water and toluene in the necessary temperature range using the equation

$$\nu = At + B/t. \quad (1)$$

These corrections have been applied to all measurements. As pointed out by Rogers *et al.* (17) the error introduced by using the intrinsic kinematic viscosity, $[\nu]$, for the intrinsic viscosity, $[\eta]$, is negligible.

Exactly 20 ml. of solution was pipetted into the viscometer and measurements of flow time were made in duplicate or triplicate until agreements within ± 0.1 sec. were obtained. Then the solution in the viscometer was diluted by the addition of 10 ml. of solvent mixture and the flow time again measured after thorough mixing. The same procedure was repeated with further additions of 10 ml. and 20 ml. of solvent mixture. Concentrations are $\frac{2}{3}$, $\frac{1}{2}$, and $\frac{1}{3}$ of the original value.

With each dilution, the flow time of the solvent was changed because of the change in the concentration of water (considering it as part of the solvent mixture). From the concentration of the solution and the latex solids, it is possible to calculate the percentage of water present in the solution. Or, alternatively, it may be determined by a Karl Fischer titration (both methods have been used by us and found to agree satisfactorily). The values of the solvent flow time corresponding to each dilution were read from a graph relating flow time to percentage composition of the solvent. After each run the viscometer was cleaned by flushing with toluene and dried carefully. It was cleaned periodically by standing overnight in concentrated nitric acid.

Solutions of the coagulated polymers were prepared by allowing about 0.25 gm. to stand overnight in toluene. They were freed of extraneous material by filtering through a sintered glass filter, porosity C, and the concentration determined in a manner similar to the vistex solutions. The viscosity measurements were made as described above. The nonpolymer corrections were assumed to be similar to those used in the vistex method. This appears to be true for GR-S, within the experimental error.

The solvents used in these measurements were both reagent grade, the toluene supplied by the Nichols Chemical Company, Toronto, Ontario, and the isopropanol by the Shell Oil Company, London, Ontario.

Preparation of Latices

Butadiene-styrene copolymers of varying average molecular weight and conversion were prepared in the Polymerization Research Laboratory under the direction of Dr. H. L. Williams.

Formula:

Butadiene (98%)	71.50 parts
Styrene	28.50 "
DDM	Variable
Water	180 parts
Emulsifier (RRC flakes—100%)	2.15 "
Potassium persulphate	0.23 "
Sodium hydroxide	to pH 10.0 - 10.5
Polymerization temperature	50° C.

The reactions were stopped with 0.16 part of hydroquinone (dissolved in water) per 100 parts of monomer. Conversions were determined on the unvented latex using a syringe, and the latices were stabilized with BLE* (1.5 parts per 100 parts by weight of dry rubber, calculated on the basis of conversion) and stripped at atmospheric pressure with live low pressure steam until there appeared to be no styrene left. The time required for stripping varied from 30 to 60 min., the actual time depending upon the conversion. During stripping, the latex reached a temperature of about 80° C. One-half of the stabilized and stripped latex was coagulated (12% brine - 0.1% sulphuric acid) and dried in an air oven. The low conversion polymers required periods of several hours drying at 40° to 50° C. High conversion samples were dried for 30 min. at 80° C.

Experimental Results and Discussion

Intrinsic Vistex Viscosity

In the usual determination of intrinsic viscosity, the solvent system remains constant in composition as the system is diluted to obtain the levels of polymer concentration necessary for extrapolation to the limiting value. However, in the determination of intrinsic vistex viscosity, where the percentage of the nonsolvent water in the latex is usually variable, the maintenance of a constant composition of solvent throughout the dilution is often difficult and did not appear to be consistent with the requirement for a rapid, precise determination. Therefore, dilution with the vistex solvent alone was attempted and the effect of variation of the percentage of water in the latex on the intrinsic vistex viscosity was examined.

Standard plant GR-S latex was added to the vistex solvent in the usual manner, then different amounts of water were added to produce a variation in the water content. At three levels of water, the vistex determination was run in the usual manner, diluting with toluene-isopropanol. Flow times for the solvent system were determined by interpolation on a plot of flow time vs. water content of a toluene-isopropanol-water (80/20/variable) system.

The intrinsic vistex viscosity values, shown in Fig. 1, were found to be independent† of the water content of the latex, within the limits where clear solutions were obtained, but the slope of the inherent vistex viscosity vs. concentration line was directly proportional to the percentage of water in the latex. This is in agreement with Tingey *et al.* (19)—this reference was discovered in a later search of the literature—who found that fractions of GR-S in benzene containing a small percentage of methanol could be diluted with pure benzene during the viscosity determination to give the true limiting value of the viscosity in pure benzene.

In further experiments, raw polymer was dissolved in the vistex solvent and the intrinsic viscosity determined, then about 1% of water was added

* BLE—an antioxidant, Naugatuck Chemical Co.

† It should be noted that the intrinsic vistex viscosity is not independent of the percentage of water in the vistex solvent (about 0.06%) that is used for dilution.

to the original vistex solution and the determination repeated, diluting with vistex solvent as above. This procedure was repeated at a number of levels of water. All the intrinsic viscosity values were identical with the first and the change of slope was similar to that shown in Fig. 1.

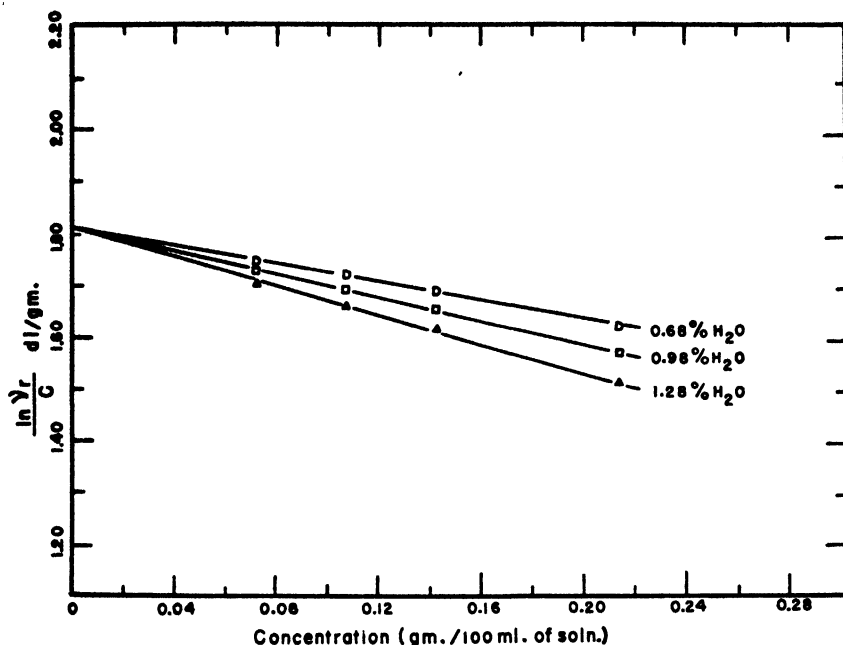


FIG. 1. Effect of amount of water in vistex solution on vistex measurements.

The basis for the method of determination of intrinsic vistex viscosity was thus established. The relation between the percentage of water and the slope of the inherent vistex viscosity vs. concentration line was used in the correction of slope data to be discussed later.

Correlation of Intrinsic Vistex Viscosity and Intrinsic Viscosity in Toluene

Several series of butadiene-styrene copolymers of varying average molecular weight* and conversion were prepared for investigation of the vistex method.

Preliminary work with the vistex method indicated normal behavior to be expected from a solution of polymer in the presence of nonsolvent.** Therefore, it was postulated that there should be a correlation between the intrinsic viscosity of the coagulated, dried polymer in toluene and the intrinsic vistex viscosity determined on the corresponding latex, providing further variables are not introduced during coagulation and drying. When this correlation is established the intrinsic vistex viscosity values may then be used to calculate viscosity average molecular weights.

* The average molecular weight was varied by the amount of modifier, dodecyl mercaptan, DDM, added. The larger the amount of mercaptan added the lower is the average molecular weight. The polymerization formula for standard GR-S contains 0.42 part of DDM.

** The literature has indicated adequate correlations of the intrinsic viscosity of polymer in a good solvent with that in a poor solvent.

As a basis for this correlation and to permit an evaluation of the variables of coagulation and drying, the intrinsic viscosities of coagulated, dried polymer in toluene were correlated with the corresponding values in toluene-isopropanol (80/20).

Intrinsic viscosities in toluene $[\nu]_T$, and in the vistex solvent, $[\nu]_{VS}$, for three series of experimental polymers are shown in Table I. When plotted on a logarithmic scale in Fig. 2 these data give a linear relation represented by the equation:—

$$\log [\nu]_T = 0.0827 + 1.08 \log [\nu]_{VS}. \quad (2)$$

TABLE I

INTRINSIC VISTEX VISCOSITIES AND CORRESPONDING INTRINSIC VISCOSITIES OF COAGULATED, DRIED POLYMER IN TOLUENE AND VISTEX SOLVENT. BUTADIENE-STYRENE COPOLYMER

No.	Parts DDM	Conv., %	Intrinsic vistex	Intrinsic viscosity	
				In toluene	In vistex solvent
<i>MM—11,3,42</i>					
3	0.40	55.1	—	1.68	1.35
4	0.45	56.0	—	1.45	1.19
5	0.50	54.2	—	1.33	1.08
6	0.60	55.3	—	1.10	0.94
<i>MM—48,1,28-48</i>					
1	0.32	23.0	1.12	1.47	1.21
2	"	27.2	1.19	1.55	1.26
3	"	40.3	1.45	1.86	1.42
4	"	48.0	1.58	2.01	1.60
5	"	57.6	1.69	2.13	1.72
6	"	65.3	1.94	2.58	2.03
7	"	75.0	2.21	2.97	2.29
8	"	82.8	1.90	2.57	2.01
<i>MM—48,4,6-54</i>					
1	0.42	18.6	1.08	1.34	1.11
2	"	25.6	1.27	1.65	1.30
3	"	42.4	1.52	1.92	1.51
4	"	57.8	1.64	2.01	1.58
5	"	67.8	1.91	2.46	2.03
6	"	73.0	1.89	2.40	1.95
7	"	76.8	2.11	2.64	2.15
8	"	81.9	2.00	2.76	2.15
X-387				2.36	1.82
Plant runs				2.37	1.88

Values for standard GR-S were found to fit this relation. A further confirmation was found in the work of Cragg and Rogers (8) who report the intrinsic viscosity of Sarnia GR-S to be 2.07 in benzene and 1.60 in benzene-isopropanol (80/20), compared with 1.64 for the latter value calculated from their $[\eta]_T = 2.07$ and Equation (2). The divergence between Cragg's value and our value of $[\nu]_T$ for GR-S is due mainly to the fact that our values are corrected for nonrubber material and to some difference in calibration methods.

A relation very similar to Equation (2) is reported by Mark *et al.* (11) for the intrinsic viscosities of polystyrene in toluene and method ethyl ketone. A review and recalculation of the data of Harris and Kolthoff (12, 14) has shown

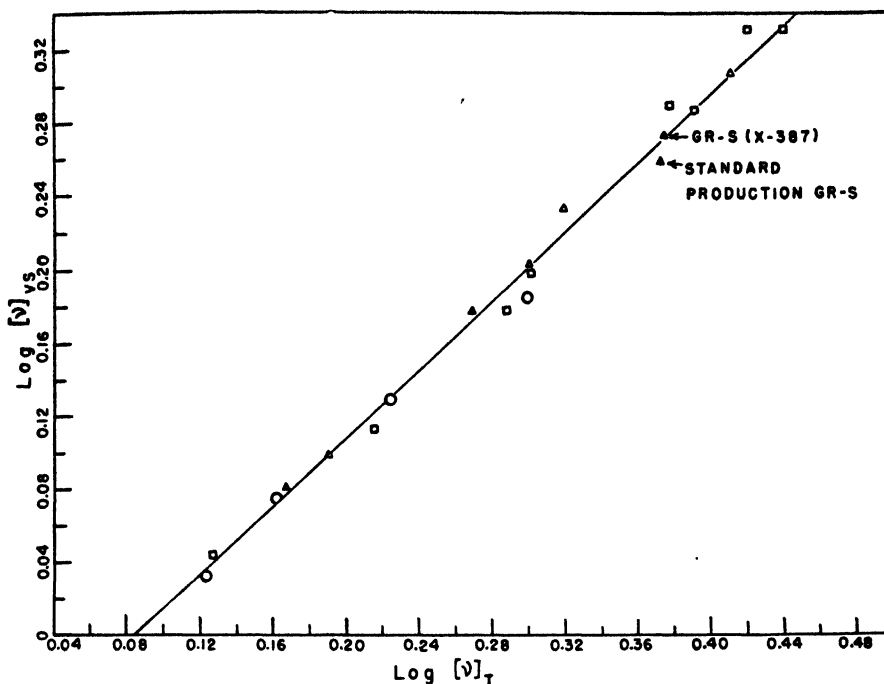


FIG. 2. Correlation between viscosity of polymer in toluene, $[\nu]_T$, and in vistex solvent, $[\nu]_{VS}$.

- charge MM-11, 3, 42
- △ charge MM-48, 1, 28-48
- charge MM-48, 4, 6-54.

approximate linear relations on logarithmic scales between the inherent viscosities in benzene and the various vistex solvents. There is, therefore, good evidence that valid viscosity - molecular weight relations may be obtained in the system toluene-isopropanol (80/20 by volume).

The correlation of intrinsic vistex viscosities and the intrinsic viscosities of the corresponding coagulated, dried polymer was then investigated. Experimental data are shown in Tables I and II and plotted in Fig. 3.

The least squares equation for these data is:—

$$\log [\nu]_T = 0.101 + 1.04 \log [\nu]_V. \quad (3)$$

Deviations of experimental points from the least squares line were considerably greater than those found for the coagulated, dried polymer, see Fig. 2. These are the result of additional variables introduced by coagulation and drying. Both negative and positive changes in $[\nu]_V$ of the same magnitude as the deviations shown in Fig. 3 have been found for latices under various conditions of aging even at low temperatures. Differences in $[\nu]_T$ or $[\nu]_V$ between Equation (2) and Equation (3) are of the order of only 0.05 dl. per

TABLE II

INTRINSIC VISTEX VISCOSITIES AND CORRESPONDING INTRINSIC VISCOSITIES OF COAGULATED, DRIED POLYMER IN TOLUENE. BUTADIENE-STYRENE COPOLYMER

No.	Parts DDM	Conversion, %	Intrinsic vistex	Intrinsic viscosity
<i>MM-48, 2, 4-49</i>				
1	0.42	20.0	—	1.24
2	"	31.6	1.14	1.36
3	"	41.4	1.19	1.53
4	"	—	—	—
5	"	69.8	1.75	2.20
6	"	75.0	2.02	2.66
7	"	80.7	2.11	2.89
8	"	82.6	2.18	2.81
9	"	87.0	1.79	2.44
10	"	93.5	1.22	—
<i>MM-48, 2, 18-50</i>				
1	0.40	66.0	1.26	2.25
2	0.48	66.6	1.54	1.93
3	0.56	67.2	1.39	1.62
4	0.64	67.6	1.05	1.38

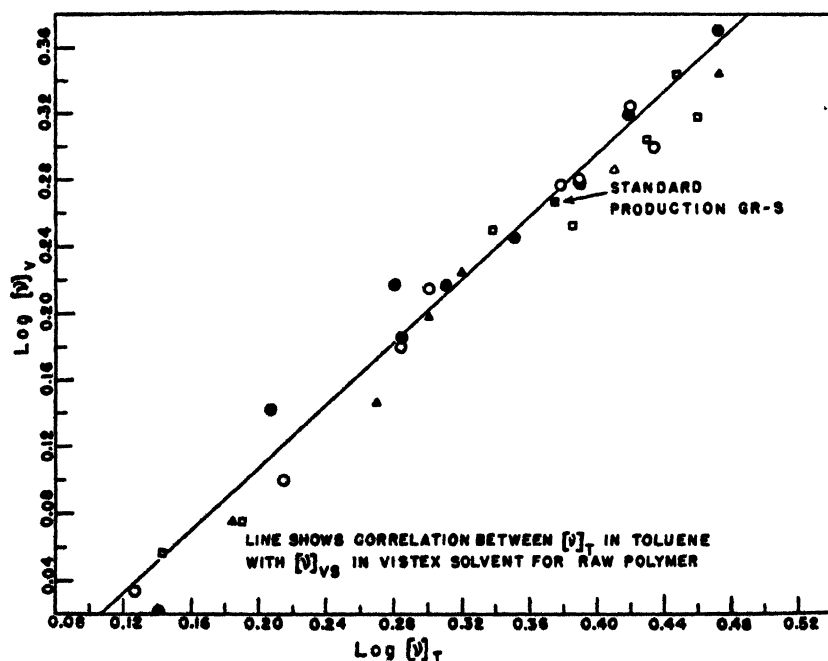


FIG. 3. Correlation between intrinsic viscosity and intrinsic vistex viscosity.

- charge *MM-48, 4, 6-54*
- charges *MM-48, 2, 19-51* and *MM-48, 2, 18-50*
- charge *MM-48, 2, 4-49*
- △ charge *MM-48, 1, 28-48*.

gm. Therefore, it is felt that Equation (2) can be used with confidence to calculate viscosity average molecular weights from intrinsic vistex viscosity data.

Vistex-Conversion Relations

The vistex method has been most widely used in the determination of vistex-conversion data. Typical intrinsic vistex viscosity - conversion and intrinsic viscosity - conversion curves are shown in Figs. 4 and 5 for varying conversions

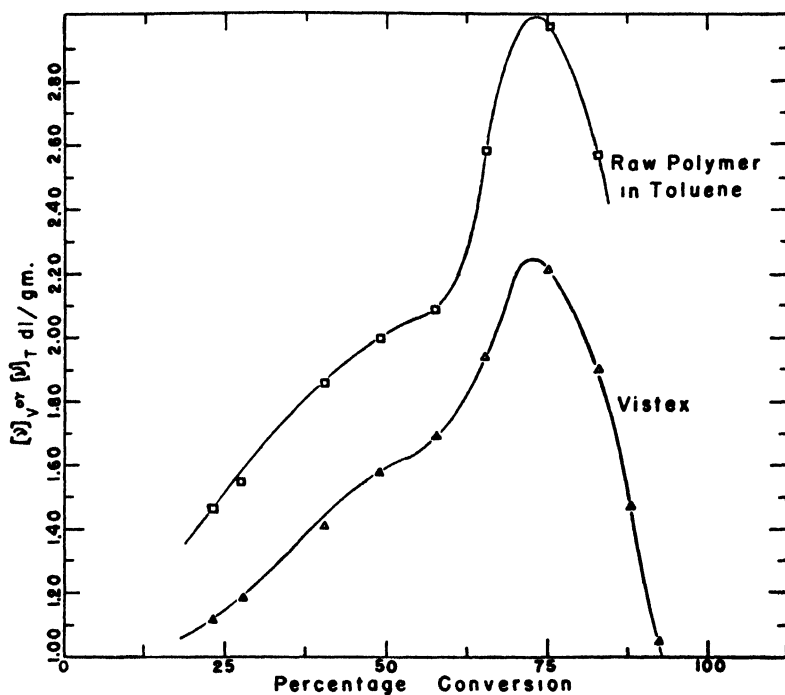


FIG. 4. Viscosity and vistex conversion curves for charge MM-48, 1, 28-48 (0.32 part DDM).

at two levels of modifier, 0.32 and 0.42 part of DDM. The maxima in the curves are very pronounced and appear to be shifted to higher conversions at higher levels of modifier, occurring at about 73% conversion for 0.32 DDM and about 80% conversion for 0.42 DDM.

The conversion level at which the maximum occurs is most commonly called the gel point. Owing to the general tendency to consider gel as detrimental to the quality of a rubber, the gel point is most frequently determined with the intention of restricting study to the system at conversions below this point or of delaying the onset of gel. Determination of the gel point is therefore, of considerable importance in polymerization research.

Although the gel point may be estimated fairly readily from vistex-conversion curves, a method of estimation of the position of a single determination relative to the gel point would be useful. One possibility of this lies in the slope of the inherent vistex viscosity vs. concentration lines.

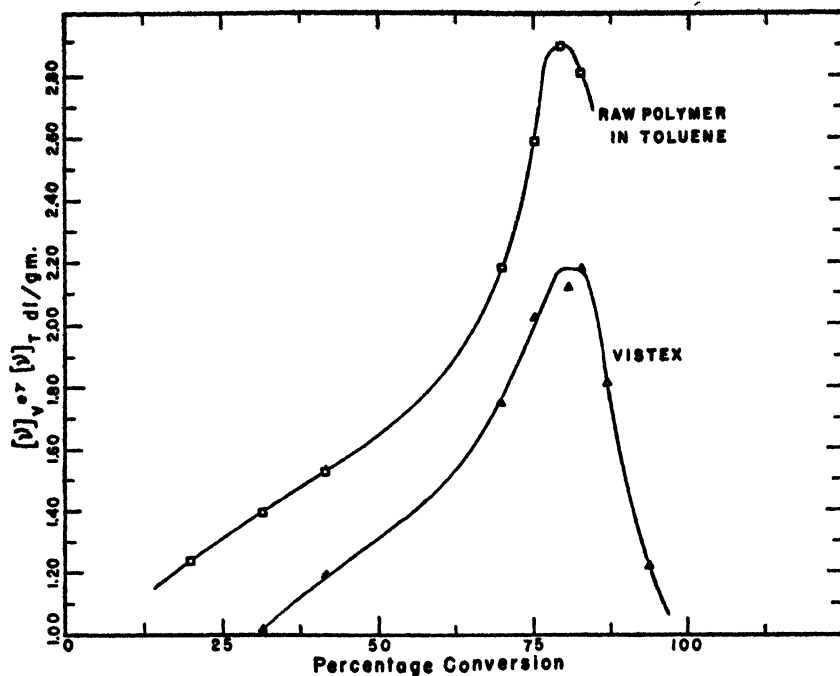


FIG. 5. Viscosity and vistex conversion curves for charge MM-48, 2, 4-49 (0.42 part DDM).

Slopes of the Inherent Viscosity vs. Concentration Lines

A typical series of lines relating the inherent vistex viscosity and concentration over a range of conversions is shown in Fig. 6. Within the limits of

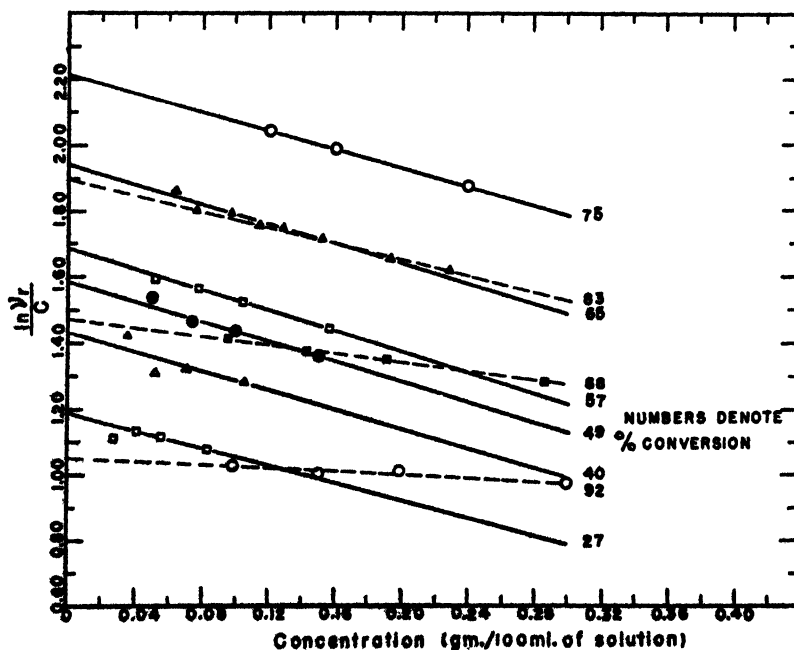


FIG. 6. Inherent vistex viscosity vs. concentration.

concentration used, the inherent vistex is related to the concentration of the polymer solution by the equation:—

$$\frac{\ln \nu_r}{c} = b - ac, \quad (4)$$

where b is the intrinsic vistex viscosity, $[\nu]_V$, while a is the slope of the line and reflects the interaction among soluté molecules. Mead and Fuoss (16) found for a wide range of fractions of polyvinyl chloride that:

$$a = \beta[\nu]^2, \quad (5)$$

where β is a constant equal to 0.14. The resulting equation,

$$\frac{\ln \nu_r}{c} = [\nu] - \beta[\nu]^2c, \quad (6)$$

has been derived by Huggins (13) from theory, using an approximation that is valid at zero concentration. However, Ewart (10) found that, when the slopes a of the inherent viscosity lines were plotted against intrinsic viscosities on a logarithmic scale, the resulting straight line had a slope considerably less than 2 for a butadiene–styrene copolymer. It was also found that the value of the exponent tended to approach 2.0 as the styrene content of the polymer increased. This suggests that the equation should be written:—

$$\frac{\ln \nu_r}{c} = [\nu] - \beta'[\nu]^nc, \quad (7)$$

where n is found experimentally for the material under investigation.

Baker (3) suggested that the slopes of the inherent viscosity lines might be used to detect gel and later (4) found that a sample of polybutadiene microgel showed strongly positive slopes and a low intrinsic viscosity. In Fig. 6 it is shown that the slopes of the lines representing polymers at high conversions, i.e., over the gel point, are distinctly less negative than those for samples of similar intrinsic viscosities at lower conversions. The same trend was found upon examination of the viscosity relations of coagulated, dried polymer in toluene. It appeared possible, therefore, that Equation (7) might be used to detect a significant change in viscosity characteristics at the gel point.

A test of Equation (7) is to plot the slope a of the inherent viscosity vs. concentration lines against intrinsic viscosity on a logarithmic scale. This plot is shown in Fig. 7 for the intrinsic vistex and for intrinsic viscosity data on the same series of polymers—varying conversion, 0.32 DDM. The slopes of the inherent vistex lines were corrected for water, using the data of Fig. 1. This correction is of the same order as that reported by Harris and Kolthoff (12) and was found to be valid in the range $[\nu]_T = 1.5$ –2.5. Values in the lower ranges of $[\nu]_V$ could not be corrected until more data on the variation of the correction for water at different values of $[\nu]_V$ are obtained.

The intrinsic viscosity data give a fairly good linear relation up to 65% conversion, with a slope n of 1.1 and $\beta' = 0.28$, i.e., the data up to 65% conversion are represented by

$$\frac{\ln \nu_r}{c} = [\nu]_T - 0.28[\nu]_T^{1.1}c. \quad (8)$$

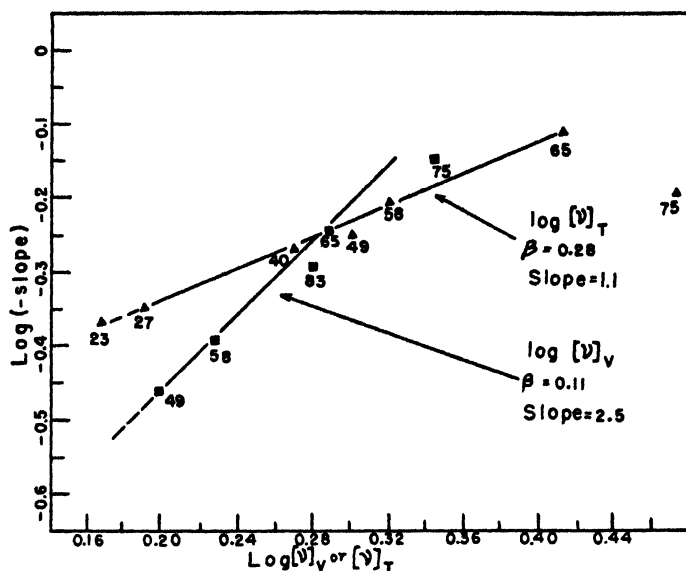


FIG. 7. Correlation between the intercept and slope of $\frac{\ln \nu_r}{c}$ vs. c for charge MM-48, 1, 28-48 (0.32 part DDM).

Above 65% conversion the values of slope a all lie below the values calculated from Equation (8) and this becomes very pronounced above 75% conversion. Values of β' calculated from Equation (8) change significantly from 0.28 at 65% conversion to 0.19 at 75% conversion. The change in β' correlates well with the onset of gelation in this case.

Intrinsic vistex viscosity data shown also in Fig. 7 follow the same general trends and may be represented, up to 65% conversion, by the equation:—

$$\frac{\ln \nu_r}{c} = [\nu]_V - 0.11[\nu]_V^{2.5}c. \quad (9)$$

Data for the intrinsic viscosities of coagulated, dried polymer in the toluene-isopropanol (80/20) can also be represented by Equation (9). As might be expected, the relative change in calculated values of β' in the region of the gel point is much smaller in magnitude than that shown by polymer in toluene. However, the decrease in β' is still detectable at 75% conversion. Similar effects have been found in unpublished work on the viscosity relations of fractions of GR-S in toluene. The changes in the relations were tentatively ascribed to an increase in the branched structure of the molecule. The higher values of the exponent n in Equation (9) are apparently caused by the addition of nonsolvent. Mark *et al.* (11) have reported values of intrinsic viscosities,

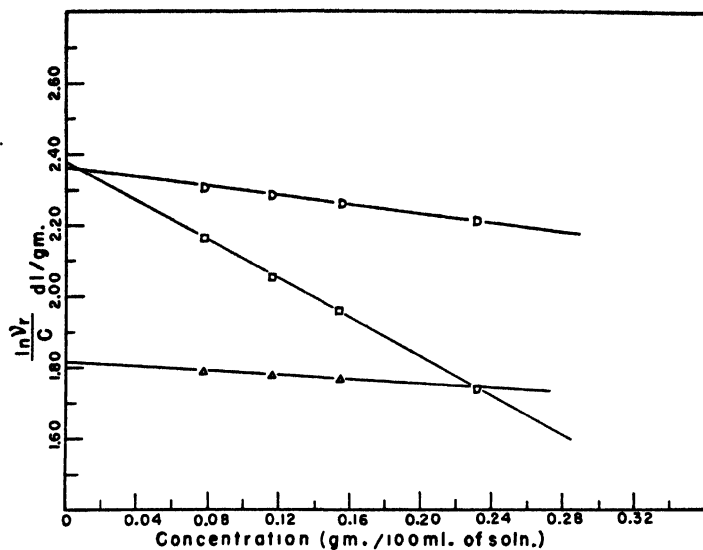


FIG. 8. $\frac{\ln v_r}{c}$ vs. c for coagulated, dried polymer.

- In toluene, diluting with toluene.
- △ In toluene-isopropanol (80/20), diluting with same.
- In toluene-isopropanol (80/20), diluting with toluene.

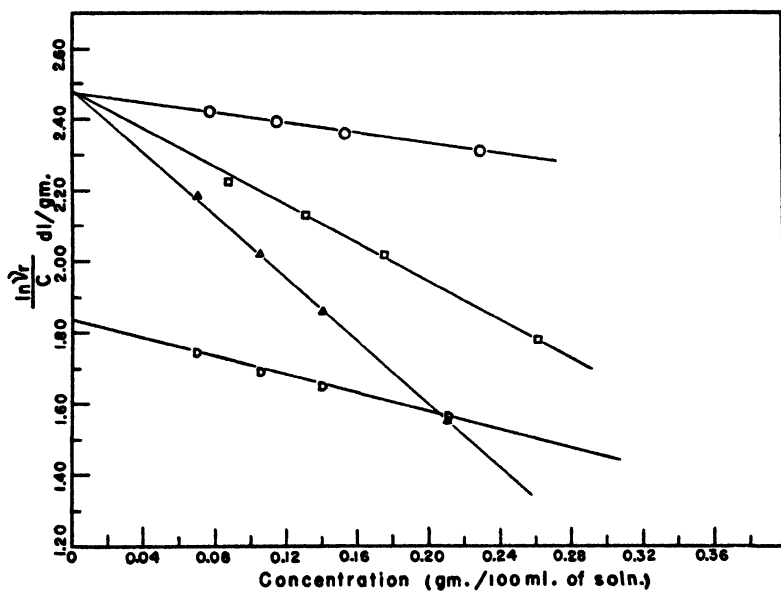


FIG. 9. $\frac{\ln v_r}{c}$ vs. c for polymer and latex solutions

- Polymer in toluene, diluting with toluene.
- Polymer in toluene-isopropanol (80/20), diluting with toluene.
- △ Latex in toluene-isopropanol, diluting with toluene.
- ◇ Latex in toluene-isopropanol, diluting with toluene-isopropanol.

slopes of the reduced specific viscosity vs. concentration lines, and values of k' calculated from the Huggins-Kraemer relation,

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad (10)$$

for fractions of polystyrene in toluene and methyl ethyl ketone (MEK). Values of k' for polymer in MEK were higher than those found with toluene and were not constant over the range of molecular weights when calculated from Equation (10). However, recalculation of the data has shown that the exponent is no longer equal to 2 for the MEK system. Substitution of the corrected value of the exponent in Equation (10) results in fairly constant values of k' . We are unable to compare the changes in exponent caused by addition of nonsolvent to that shown by our data because Mark's viscosity values for polymer in MEK were obtained at a higher temperature than those in the toluene system.

Other comparative data for whole polymers do not appear to be available in the literature. However, equations of this type have not been tested extensively for whole polymers, probably because it has been reported (18) that the values of slopes a of the inherent viscosity lines are affected by the heterogeneity of molecular weight distributions.

It is interesting, nevertheless, to note that the reduction in β' caused by the presence of 20% by volume of isopropanol, cf. Equations (8) and (9), is of the same order as the reduction of β caused by the addition of 20% by volume of butanol to a toluene solution of polystyrene reported by Alfrey *et al.* (2). The available data are not extensive enough to be used as a basis for correlation of β' and n with structural changes but they do suggest possibilities for further research.

Dilution with Pure Solvent

The data of Fig. 1 suggest that the vistex solution might be diluted with a pure solvent such as toluene and, by the use of the appropriate solvent flow times, the intrinsic viscosity in pure solvent obtained by extrapolation. This was found to be possible, as shown in Figs. 8 and 9. Excellent agreement between the intrinsic viscosities of coagulated, dried polymer in toluene and those of polymer and of latex in vistex solvent, diluting with pure toluene, were found at these viscosity levels. Although this method has a disadvantage in the greater slope for the inherent vistex line, it offers some interesting possibilities in polymerization research.

Acknowledgments

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NOTE ON THE THEORY OF ELECTROLYTIC DOUBLE LAYERS¹

BY A. J. DEKKER

Abstract

The mechanism suggested by Gurney for the formation of a double layer at the interface of a metal and a solution containing its ions is applied to a diffuse double layer. The diffuse part of the double layer is treated in a way that differs from Stern's method, leading to a more convenient formula for the potential ψ_δ of the diffuse part. Numerical values and a comparison with Stern's results are given.

1. Introduction

If a metal is dipped into an electrolytic solution, an electric double layer is generally formed. In the old theory of Helmholtz it was assumed that the metal acquired a surface charge, thus forming a molecular condenser with ions of opposite charge in the solution which are adsorbed on the metal. According to this theory, the whole potential difference between metal and bulk solution is confined to this nondiffuse double layer, and the capacity is given by $C_0 = \epsilon'/4\pi\delta$, where δ is of the order of an ionic radius and ϵ' is the dielectric constant of the layer. From experimental results it is known that C_0 is of the order of magnitude of $20\mu\text{f.}$ for an electrode of 1 cm.^2 It is difficult to assign a physical meaning to ϵ' and so it is perhaps better to speak about an effective distance $\delta_{\text{eff.}} = \delta/\epsilon'$ of the plates, referred to vacuum.

The idea of a diffuse double layer was first conceived by Gouy and Chapman to take into account the thermal motion of the ions and the diffusion resulting from it. Using Poisson's equation and a Boltzmann distribution, a relation between the surface charge σ_0 on the metal and the total potential drop ψ_0 is obtained. Owing to the fact that they consider the ions as pointlike particles, the calculated capacities are too high by a factor of about 10.

To account for the finite size of the ions, Stern (2) combined the foregoing ideas. According to him the total potential drop takes place in two stages: the first stage lies between $0 < x < \delta$ (see Fig. 1, c) and is commonly called "Stern layer", the second is a diffuse part in the region $x > \delta$ (Gouy layer). The value of δ is again of the order of an ionic radius. We so arrive at three representations (see Fig. 1), of which for the case of electrolytes Stern's is doubtless the best. There is, however, one point that we think is not completely satisfactory; Stern divides the Gouy layer into two parts, one being a surface charge at $x = \delta$ and the other part being really diffuse for $x > \delta$; the reason for this is not quite clear and we will see in Section 3 that a more convenient expression is obtained by considering the diffuse part as a whole.

As far as the mechanism of formation of a double layer is concerned, a theory has been put forward by Gurney (1) for the case of a metal dipped into a

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Contribution from the Department of Physics, The University of British Columbia, Vancouver, Canada.

solution containing its own ions. This mechanism is based on the assumption that the exchange of positive ions between metal and solution takes place by quantum-mechanical tunnel effect. If we apply this mechanism to a diffuse double layer, we obtain nearly the same result given by Gurney; this will be shown in Section 2.

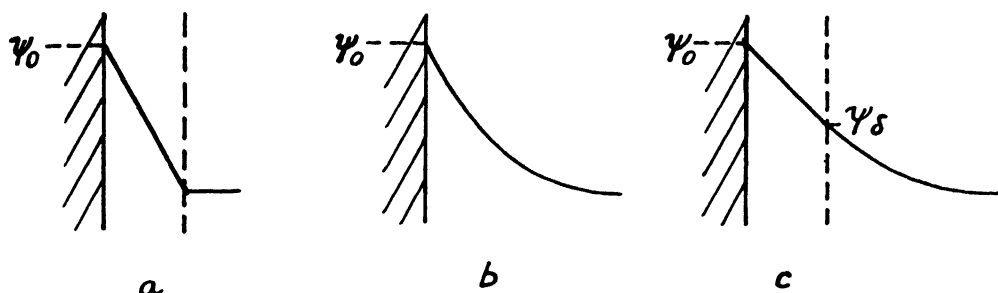


FIG. 1. Three representations of an electrolytic double layer

- a. Helmholtz
- b. Gouy-Chapman
- c. Stern

2. Calculation of ψ_0

Following Gurney's suggestion we will denote the energy of an ion on the metal surface in the ground state by Y_0 ; the energy of an ion at infinity will be taken as zero and the energies below zero will be counted as positive throughout this note. For a metal in vacuum, Y_0 is approximately equal to the sum of the sublimation and ionization energy minus the work function of the metal. The ground state of a hydrated metal ion in the solution will be denoted by W_0 ; for the moment we will assume that the metal ions are hydrated by one water molecule only. A complete description of the exchange mechanism between metal and solution is given by Gurney (1). The exchange process in each individual case will not always take place at the same distance between an occupied level on the metal and a vacant level in the solution, but we will assume an average distance δ . We will also assume that the negative ions in the solution do not approach the metal any closer than δ and hence in this model there is no space charge in the region $0 < x < \delta$, in accordance with Stern's idea.

Suppose now that in the equilibrium state, for which the number of ions going into solution is equal to the number deposited, the total potential drop between metal and bulk solution is ψ_0 , where ψ_0 has the sign corresponding to the metal. Referred to the energy levels in the bulk solution, the ground state of an ion on the metal surface will then have changed into $(Y_0 - e\psi_0)$ and hence the fraction of surface ions with energies between E and $E + dE$ is for a Boltzmann distribution given by:*

$$\exp. (E - Y_0 + e\psi_0)/kT \cdot dE/kT.$$

* We consider monovalent ions throughout.

In the same way the fraction of hydrated ions at $x = \delta$ having energies in the same range will be equal to

$$\exp. (E - W_0 + e\psi_\delta)/kT \cdot dE/kT.$$

If N_w is the number of water molecules at $x = \delta$ per unit area opposite the metal and N_δ^+ the corresponding quantity for the positive ions, we obtain the equilibrium condition

$$N_w p_s(E) \exp. (E - Y_0 + e\psi_0)/kT \cdot dE/kT \\ = N_\delta^+ p_d(E) \exp. (E - W_0 + e\psi_\delta)/kT \cdot dE/kT \quad (1)$$

Here $p_s(E)$ is the probability that a surface ion with energy E will jump to a corresponding level in the solution per unit time; $p_d(E)$ is the corresponding term for deposition. The ratio $p_d/p_s = \beta$ will actually be a function of E , but the process of exchange will take place in a very narrow band of energies and will be treated as a constant; β is probably of the order of 1.*

We will now define the concentration of the bulk solution as

$$c_\infty = \text{moles of salt/moles of water.}$$

Writing $c_\delta^+ = N_\delta^+/N_w = n_\delta^+/n_{w\delta}$, where n refers to numbers per unit volume, it can easily be seen that if we assume the number of water molecules per unit volume to be approximately the same for $x = \delta$ as for $x = \infty$,

$$c_\delta^+ \simeq c_\infty e^{-e\psi_\delta/kT}. \quad (2)$$

Expressions (1) and (2) lead to the result

$$e\psi_0 \simeq Y_0 - W_0 + kT \log \beta c_\infty. \quad (3)$$

This result is the same as that obtained by Gurney, except for the slight approximation just mentioned.

To correct for the fact that a positive ion probably polarizes more than one water molecule, we could introduce a correction similar to that introduced by Gurney. Suppose each positive ion is on the average hydrated by p water molecules. In this case N_w in Equation (1) should be replaced by $(N_w - pN_\delta^+)$ and the factor βc_∞ in Equation (3) by $\beta c_\infty / (1 - pc_\delta^+) \simeq \beta c_\infty e^{pc_\delta^+}$. Defining $\log f^+ = pc_\delta^+$ we would find instead of Equation (3)

$$e\psi_0 = Y_0 - W_0 + kT \log \beta f^+ c_\infty. \quad (3a)$$

For $c_\delta^+ \rightarrow 0$, f^+ approaches 1. This case is different from that of a non-diffuse double layer inasmuch as in the latter case the "activity coefficient" would be defined by $\log f = pc_\infty$ (see Gurney). The relation between f^+ and f is apparently

$$\log f^+ = e^{-e\psi_\delta/kT} \log f.$$

For $e\psi_\delta \gg kT$ the difference between f^+ and f becomes appreciable, but as far as the value of ψ_0 is concerned, the term $kT \log \beta f^+ c_\infty$ is generally small compared with $(Y_0 - W_0)$ and the correction for the value of ψ_0 in this case

* A more detailed statistical treatment of this equilibrium between a metal and an ionic atmosphere is given by Fowler in an appendix to Gurney's article.

will be small. Considering some numerical values, let us suppose $p = 3$. Then in a 1 normal solution $c_\infty \simeq 1/55$ and $\log f = 0.055$; the uncorrected term in Equation (3) would give

$$kT \log \beta c_\infty \simeq -4kT.$$

For positive values of ψ_δ the factor $e^{-\psi_\delta/kT}$ is always smaller than 1 and this will lead to $\log f^+ < \log f$ and hence a correction of about 1% or less. If ψ_δ is negative, as could conceivably happen in certain cases, the correction becomes larger and will depend on the ratio $e\psi_\delta/kT$. Taking $\psi_\delta = 0.1$ volt, one would get $kT \log \beta c_\infty \simeq -4kT$ instead of

$$kT \log \beta f^+ c_\infty \simeq -kT,$$

or in other words a total correction of $3kT$ for $e\psi_0$. However, in concentrated solutions, the value of ψ_δ for a given value of ψ_0 is always smaller than in diluted solutions, and this effect depresses this correction further.

3. Calculation of ψ_δ

In the Stern layer, between $x = 0$ and $x = \delta$ we have

$$\frac{d^2\psi}{dx^2} = 0; \text{ hence } \psi_0 - \psi_\delta = \frac{4\pi\delta}{\epsilon'} \sigma_0,$$

where σ_0 is the surface charge-density on the metal. Here, as already remarked in the introduction, it is perhaps better to introduce an effective plate distance $\delta_{eff} = \delta/\epsilon'$. For the region $x > \delta$ Poisson's equation gives

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon} \rho(x);$$

in this whole region we will assume a constant value of ϵ .

Writing n_∞ for the number of ions of each type per unit volume in the bulk solution, this equation becomes

$$\frac{d^2\psi}{dx^2} = \frac{8\pi n_\infty e}{\epsilon} \sinh \frac{e\psi}{kT}.$$

Multiplying both sides by $\frac{d\psi}{dx} dx$, this leads on integration to

$$\frac{d\psi}{dx} = -\left(\frac{32\pi n_\infty kT}{\epsilon}\right)^{\frac{1}{2}} \sinh \frac{e\psi}{2kT}. \quad (4)$$

To find an expression for ψ_δ we can make use of the relation

$$\int_\delta^\infty \rho(x) dx = -\sigma_0$$

or

$$2en_\infty \int_\delta^\infty \left(\sinh \frac{e\psi}{kT}\right) dx = \sigma_0 \quad (5)$$

Introducing in Equation (5) $d\psi$ instead of dx by means of Equation (4) and integrating leads to the following expression

$$\sigma_0 = \left(\frac{n_{\infty} k T \epsilon}{2\pi} \right)^{\frac{1}{2}} \cdot 2 \sinh \frac{e\psi_0}{2kT}. \quad (6)$$

We can now eliminate σ_0 , giving

$$\psi_0 - \psi_s = 8\pi \delta_{eff} \left(\frac{n_{\infty} k T \epsilon}{2\pi} \right)^{\frac{1}{2}} \sinh \frac{e\psi_0}{2kT}. \quad (7)$$

This expression is, as a matter of fact, completely independent of the way in which ψ_0 is determined. In the case of a metal in a solution of its ions, ψ_0 is determined by Equation (3); in other cases ψ_0 can be determined by an electronic equilibrium in the same way as for instance in the case of a metal in contact with an insulator or semiconductor.

Equation (7) enables us to calculate ψ_s for a given value of ψ_0 as a function of the concentration of the bulk solution. Instead of one term at the right-hand side of Equation (7), Stern obtains two terms because he divides the diffuse layer into two parts; we think, however, that it is more consistent not to do this.

4. Numerical Examples

Starting from Equation (7) we will give some numerical values of ψ_0 calculated for a given ψ_s and concentration. To be able to compare the results with those of Stern, we will take the same value, $C_0 = 1/4\pi\delta_{eff} = 2.6 \times 10^7$ cm., that he used. This value is taken from the work of Krueger and Krumreich* on the electrocapillary curve of the system mercury-1 normal potassium nitrate: from their measurements it can be concluded that the capacity of this system is independent of ψ_0 , or, in other words, that the diffuse part of the double layer is negligible compared with the Stern layer. Assuming $\epsilon = 81$ we find on inserting the various constants into Equation (7) for the potential difference expressed in volts that

$$\psi_0 - \psi_s = 0.42 \sinh \frac{e\psi_0}{2kT} \quad \text{for a 1 normal solution}$$

$$\psi_0 - \psi_s = 0.042 \sinh \frac{e\psi_0}{2kT} \quad \text{a 0.01 normal solution.}$$

Some results are given in Table I; Stern's corresponding values are included (S). As far as the capacity $C = \sigma_0/\psi_0$ of the diffuse layer is concerned, we see that because $\psi_0 - \psi_s = 4\pi\delta_{eff}\sigma_0$ and $C_0 = 1/4\pi\delta_{eff}$ (being the capacity of a flat layer), $C = C_0(1 - \psi_s/\psi_0)$. Hence, C is 100 ψ_s/ψ_0 % less than C_0 . These percentages are also included in the table.

The conclusions that can be drawn from this table are qualitatively the same as those obtained from Stern's more complicated formula. At higher concentrations the double layer becomes flatter and in a 1 normal solution the capacity is only slightly dependent on ψ_0 ; in dilute solutions, however,

* See Stern (2).

TABLE I
NUMERICAL RESULTS (SEE TEXT)

ψ_δ	1 normal solution				0.01 normal solution			
	ψ_0		$100 \psi_\delta / \psi_0$		ψ_0		$100 \psi_\delta / \psi_0$	
0.025	0.24	—	10	—	0.047	—	53	—
0.05	0.54	S 1.06	9.3	S 4.5	0.10	—	50	—
0.10	2.0	—	5.0	—	0.25	S .302	40	S 33
0.15	—	—	—	—	0.57	S .914	26	S 16.4
0.20	—	—	—	—	1.33	—	15	—

the capacity is strongly dependent on ψ_0 , and especially for small values of ψ_0 the difference between C and C_0 is appreciable. In general, Stern's values of ψ_δ corresponding to the same ψ_0 are smaller than those obtained from Equation (7). We do not think it possible at the moment, however, to decide which agree best with the experiments.

Acknowledgment

The author is indebted to Dr. W. Opechowski for valuable discussion.

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APPLICATION DE LA RÉACTION DE MEERWEIN À LA BENZALACÉTONE¹

PAR PHILIBERT L'ÉCUYER ET CHARLES-A. OLIVIER²

Sommaire

La réaction de Meerwein entre divers sels de diazonium aromatiques substitués et la benzalacétone a donné naissance aux dérivés de l' α -acétylstilbène suivants: l' α -acétyl-4-bromostilbène, l' α -acétyl-4-chlorostilbène, l' α -acétyl-3-nitrostilbène et l' α -acétyl-4-nitrostilbène. D'autre part la même réaction entre la benzalacétone et d'autres sels de diazonium aromatiques substitués a conduit aux dérivés du dibenzyle suivants: l' α -acétyl- β -chloro-2-chlorodibenzyle, l' α -acétyl- β -chloro-3-chlorodibenzyle, l' α -acétyl- β -chloro-2-méthyldibenzyle, l' α -acétyl- β -chloro-3-méthyldibenzyle, l' α -acétyl- β -chloro-2-nitrodibenzyle et l' α -acétyl- β -chloro-4-phényldibenzyle. Le sel de diazonium de la *p*-nitraniline et l'acide 2-furfurylacrylique ont donné naissance à l' α -(4-nitrophényl)- β -(2-furfuryl)éthène. L'action du même sel de diazonium sur le *p*-nitrocinnamitrile a fourni l' α -cyano-4,4'-dinitrostilbène. Enfin l'hydrolyse de l' α -chloro-4-chlorohydrocinnamitrile a donné l'acide α -chloro-4-chlorohydrocinnamique et finalement l'acide 4-chlorocinnamique par l'élimination de HCl.

Introduction

Meerwein et ses collaborateurs (12) ont montré que l'action des chlorures de diazonium aromatiques sur les composés carbonyles possédant une double liaison entre les carbones α et β conduit à la synthèse de dérivés du stilbène. Avec les aldéhydes, les nitriles et les acides aromatiques α , β -non saturés le groupement phényle, qui est introduit par l'intermédiaire du sel de diazonium, se fixe sur le carbone α de la double liaison oléfinique (1, 2, 3, 4, 5, 10, 12) et les produits de la réaction sont des dérivés non-saturés du stilbène. Par contre, lorsque la condensation se fait avec les esters aromatiques, HCl s'additionne à la double liaison au cours de la réaction et les composés obtenus sont saturés. Dans les mêmes conditions, les chlorures de diazonium aromatiques réagissent également avec l'acrylate de méthyle et l'acrylonitrile (9). Dans ce dernier cas cependant le groupement phényle se fixe sur l'atome de carbone β du composé non-saturé au lieu de se joindre à l'atome de carbone α , pendant que HCl s'additionne sur la même liaison éthylénique.

Dans une étude précédente (11) il a été constaté que la réaction de Meerwein peut s'effectuer entre des amines aromatiques substituées et des acides aromatiques non-saturés également substitués. Cette condensation fournit une

¹ *Manuscrit reçu le 25 mars 1949.*

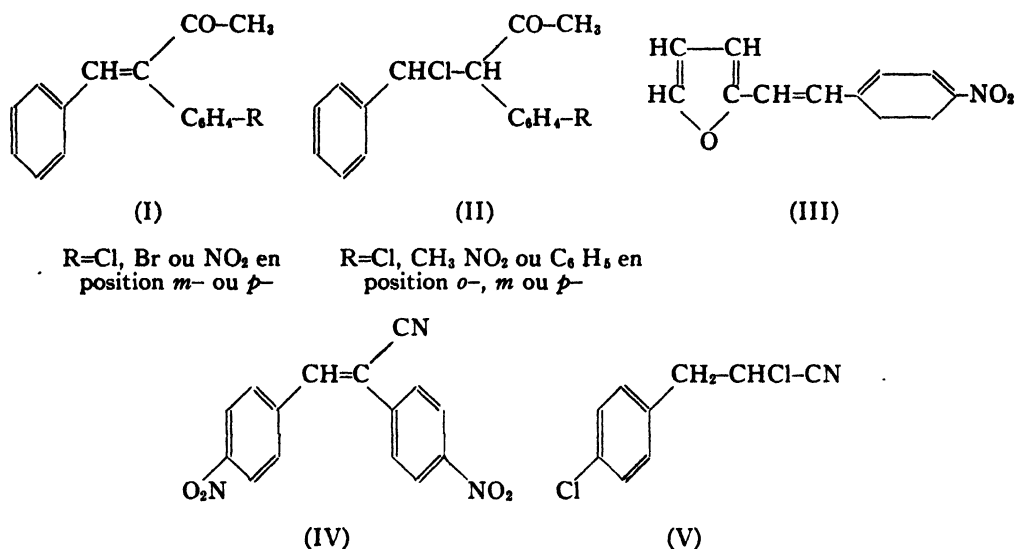
Contribution du Département de chimie de l'Université Laval, Québec (Qué.).

² *Boursier du Conseil National des Recherches.*

méthode satisfaisante pour la préparation des dérivés du stilbène avec des groupements substituants dans n'importe quelle position des deux anneaux du benzène.

En raison de l'intérêt qu'offre certains composés du stilbène possédant des substituants dans la partie aliphatique de la molécule en même temps que dans les anneaux benzéniques, nous avons cru bon d'étudier la possibilité d'appliquer la réaction de Meerwein à la benzalacétone et à ses dérivés.

La condensation entre la benzalacétone et les sels de diazonium de quatre amines aromatiques: la *p*-bromaniline, la *p*-chloraniline, la *m*- et la *p*-nitranilines, se passe normalement. Le groupement phényle se fixe sur l'atome de carbone non-saturé α pour donner les quatre dérivés α -acétylés du stilbène: α -acétyl-4-bromostilbène, α -acétyl-4-chlorostilbène, α -acétyl-3-nitrostilbène et α -acétyl-4-nitrostilbène (I).



Toutefois avec d'autres amines aromatiques substituées l'*o*- et la *m*-chloraniline, l'*o*- et la *m*-toluidine, l'*o*-nitraniline et le *p*-aminodiphényle les composés qui ont été isolés étaient les dérivés du dibenzyle suivants: α -acétyl- β -chloro-2-chlorodibenzyle, α -acétyl- β -chloro-3-chlorodibenzyle, α -acétyl- β -chloro-2-méthyldibenzyle, α -acétyl- β -chloro-3-méthyldibenzyle, α -acétyl- β -chloro-2-nitrodibenzyle et α -acétyl- β -chloro-4-phényldibenzyle (II), HCl s'étant additionné à la double liaison. Il est difficile d'expliquer pourquoi HCl s'additionne à la double liaison, dans certains cas, tandis qu'il ne le fait pas dans d'autres. Nous avons pu constater cependant que dans les composés chlorés HCl n'est pas solidement fixé à la molécule et qu'il se dégage lorsque la substance est chauffée au-dessus de son point de fusion à la pression atmosphérique.

Nous avons tenté la condensation de la *m*-nitrobenzalacétone et de la *p*-nitraniline. La réaction semble se passer normalement, mais il fut impossible de purifier le produit obtenu. Par cristallisation, de beaux cristaux

se formaient alors que la solution était encore chaude, mais au cours du refroidissement une substance goudronneuse se déposait inévitablement sur eux et les faisait se ramollir. Il semble donc qu'il y a trop peu de différence entre les propriétés physiques des substances en présence pour permettre une purification convenable. Après une réaction de Meerwein on retrouve toujours inchangée une certaine quantité du composé carbonyle non-saturé. Comme le point d'ébullition de la benzalacétone substituée est trop près de celui du composé synthétisé, il est impossible d'éliminer la première par la distillation dans le vide. Il semble aussi que la solubilité des deux substances dans les solvants organiques ordinaires soit trop voisine pour en permettre la purification par la cristallisation. Pour ces raisons il nous a paru inutile de tenter la condensation de Meerwein entre d'autres benzalacétones substituées et les sels de diazonium aromatiques.

Incidentement, comme nous disposions d'une certaine quantité d'acide furfurylacrylique, nous avons tenté sa réaction avec la *p*-nitraniline et l' α -(4-nitrophényl)- β -(2-furfuryl)-éthylène (III) a été isolé de la façon habituelle. Depuis la communication de nos résultats au Conseil National des Recherches la même préparation a été décrite par Brown et Kon (6).

Nous avons pu vérifier après Koelsch (9) que, dans l'application de la réaction de Meerwein à l'acrylonitrile, le groupement aryle entre en position β et qu'il y a en même temps addition de HCl sur la double liaison le chlore se fixant sur le carbone α . Pour obtenir les dérivés de l' α -cyanostilbène correspondants il faut donc éliminer une molécule d'acide chlorhydrique sous l'action de la pipéridine. C'est ainsi que, après une première condensation de la *p*-nitraniline avec l'acrylonitrile et l'élimination de HCl à l'aide de la pipéridine pour donner naissance au *p*-nitrocinnamonitrile nous avons obtenu par la réaction de ce dernier avec le sel de diazonium de la nitraniline, le 4,4'-dinitro- α -cyanostilbène (IV).

La réaction avec l'acrylonitrile offre aussi la possibilité de préparer des acides α -chlorocinnamiques. Il suffit d'hydrolyser en milieu chlorhydrique les α -chlorohydrocinnamonitriles (V) pour les obtenir.

Partie Expérimentale

Toutes les réactions rapportées ici ont été effectuées à partir de 0.1 mole d'amine et d'une quantité équimoléculaire du composé carbonyle. La quantité des autres substances nécessaires à la réaction demeure constante pour cette quantité de réactifs. Quant au solvant, l'acétone, il faut en mettre une quantité suffisante pour maintenir le composé carbonyle en solution.

Un mélange d'amine (0.1 mole), d'acide chlorhydrique à 25% (50 ml.) et de glace (50 g.) est diazoté à une température inférieure à 5° C. par l'addition graduelle d'une solution de nitrite de sodium (8.4 g.) dans l'eau (16 ml.). Le chlorure de diazonium ainsi formé est versé dans un mélange refroidi du composé carbonyle α , β -non saturé (0.1 mole) dissous dans l'acétone et

d'acétate de sodium anhydre (25 g.). L'addition d'une solution de chlorure cuivrique dihydraté (4.2 g.) dans l'eau (12 ml.) catalyse la réaction.

Celle-ci qui est caractérisée par un dégagement de gaz assez rapide, s'amorce à une température qui varie suivant les réactifs. Dans la plupart des cas la réaction débute à une température inférieure à 15° C., mais il est quelquefois nécessaire de plonger le mélange réactionnel dans un bain d'eau chaude pour l'amorcer. De toute façon une fois la réaction amorcée, elle est assez exothermique pour que la température se maintienne sans chauffage. Pendant tout le temps que dure la réaction (environ deux heures) le mélange est soumis à une vigoureuse agitation mécanique.

On soumet le tout à une distillation à la vapeur d'eau pour récupérer l'acétone et chasser les composés volatils formés pendant la réaction. On rend le résidu alcalin à l'ammoniaque, on décante la liqueur surnageante et on lave la gomme qui reste plusieurs fois à l'eau pour éliminer les dernières traces de cuivre. La gomme est ensuite dissoute dans le chloroforme ou l'éther, la solution est séchée sur du sulfate anhydre de sodium et le solvant est évaporé. Le résidu est enfin soumis à la distillation dans le vide (0.005 mm.). Le composé carbonyle non transformé passe d'abord (la benzalacétone à 80°–90° C.) et le produit de la réaction est ensuite recueilli à une température plus élevée et est cristallisé de l'alcool dilué de 80 à 95% suivant le cas.

Les principales particularités des diverses condensations et quelques propriétés physiques des substances synthétisées sont contenues dans le tableau I.

TABLEAU I
SUBSTANCES PRÉPARÉES

Réactifs		Produit de réaction	P.e. ° C. (0.005 mm.)	P.f. ° C.*	Rend., %	Analyse	
Composé carbonyle	Amine					Calculé	Trouvé
Benzalacétone	<i>p</i> -Nitraniline	I 4-NO ₂	—	147	39	N = 5.3	N = 5.4
"	<i>m</i> -Nitraniline	" 3-NO ₂	150-160	98	18	N = 5.3	N = 5.2
"	<i>p</i> -Chloraniline	" 4-Cl	130-135	105-106 (13)	45	Cl = 13.8	Cl = 13.9
"	<i>p</i> -Bromaniline	" 4-Br	140-150	137-139	10	Br = 26.5	Br = 26.1
"	<i>o</i> -Chloraniline	II 2-Cl	120-125	113-114	20	Cl = 24.2	Cl = 24.4
"	<i>m</i> -Chloraniline	" 3-Cl	125-130	90-91	39	Cl = 24.2	Cl = 24.2
"	<i>o</i> -Toluidine	" 2-CH ₃	105-115	108-109	15	Cl = 13.0	Cl = 13.5†
"	<i>m</i> -Toluidine	" 3-CH ₃	115-125	70-71	20	Cl = 13.0	Cl = 13.1
"	<i>o</i> -Nitraniline	" 2-NO ₂	140-150	145-147 (déc.)	38	N = 9.2	N = 9.4
"	<i>p</i> -Phénylaniline	" 4-C ₆ H ₅	—	141-142	20	Cl = 11.7	Cl = 12.2
Ac. 2-furfurylacri- lique	<i>p</i> -Nitraniline	III —	140-145 (sub.)	129-130	23	Cl = 10.6	Cl = 10.7‡
4-NO ₂ -cinnamoni- trile	"	IV —	—	214-215†	12	N = 6.5	N = 6.7
Acrylonitrile	<i>p</i> -Chloraniline	V —	75	—	37	N = 14.2	N = 13.9
						Cl = 35.5	Cl = 35.6

* Températures non corrigées.

† Freund (7) donne 215° C. comme point de fusion du 4,4'-dinitro- α -cyanostilbène.

‡ et § Seul l'azote ou le chlore a été déterminé sauf pour ces deux composés dont l'analyse a donné respectivement les résultats suivants: Calc. C = 78.9; H = 5.7. Trouvé: C = 79.0; H = 6.2. Calc. C = 74.9; H = 6.2. Trouvé: C = 74.6; H = 6.7.

Dans deux cas, à savoir ceux de l' α -acétyl-4-nitrostilbène et de l' α -acétyl- β -chloro-4-phényldibenzyle, la gomme obtenue après la distillation à la vapeur au lieu d'être dissoute dans le chloroforme a été triturée à l'acide acétique et le solide cristallisé, la première substance de l'alcool à 95% (décoloration au noir animal) et la deuxième de l'acide acétique à 80% (décoloration au noir animal).

Acide α -chloro-4-chlorohydrocinnamique

L' α -chloro-4-chlorohydrocinnamonitrile (4.8 g.) obtenu par la réaction de Meerwein a été hydrolysé par l'acide chlorhydrique concentré (50 ml.) à l'ébullition pendant 15 h. L'acide α -chloro-4-chlorohydrocinnamique cristallise de l'alcool éthylique à 20% en minuscules cristaux blancs de p.f. 98° à 100° C. Rendement 80%. Calculé pour $C_9H_8O_2Cl_2$: Cl, 32.4%. Trouvé: Cl, 32.0%.

Acide α -chloro-4-chlorohydrocinnamique

L'acide α -chloro-4-chlorohydrocinnamique (3 g.) est dissous dans la pipéridine (10 ml.). Il se produit un fort dégagement de chaleur. Après avoir porté à l'ébullition on refroidit, on dilue à l'eau et on filtre. L'acide cristallise de l'alcool éthylique à 50% en petits prismes blancs de p.f. 248° à 250° C. (cf. Gabriel et Herzberg (8) p.f. 240° à 242° C.). Rendement quantitatif. Calculé pour $C_9H_7O_2Cl$: Cl, 19.45%. Trouvé: Cl, 19.8%.

Remerciements

Les auteurs désirent exprimer leur gratitude au Conseil National des Recherches pour un octroi et une Bourse de Recherches accordée à l'un d'eux (C.-A.O.) ainsi que pour la permission de publier ces résultats.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XXXII. 2,3-BUTANEDIOL FERMENTATIONS AT POISED HYDROGEN ION CONCENTRATIONS¹

BY A. C. NEISH² AND G. A. LEDINGHAM²

Abstract

The anaerobic dissimilation of glucose by *Bacillus polymyxa*, *Bacillus subtilis* (Ford's type), *Aerobacter aerogenes*, and *Serratia marcescens* was studied at poised hydrogen ion concentrations covering the range pH 5.0 to 8.0. Each fermentation was controlled within ± 0.05 pH units by automatic addition of ammonium hydroxide solutions. The hydrogen ion concentration had a marked effect on the overall rate of dissimilation and the relative yield of products that was similar for all organisms. The time required to completely ferment a medium containing 5% glucose varied from 22 hr. for *Bacillus subtilis* to 9½ hr. for *Aerobacter aerogenes* at the optimum pH, which was within the range 7.0 to 7.6. The yield of 2,3-butanediol decreases above pH 6.4, until above pH 7.6 little or none is formed, although fairly rapid breakdown of glucose is still obtained. At the same time the yield of acetoin tends to increase, while there is little change in the amount of ethanol formed. The yields of acetic and lactic acids increase markedly in alkaline media, the latter showing an optimum at pH 7.6. A pronounced decrease in the yields of carbon dioxide and hydrogen occurs above pH 7.0 and is accompanied by an approximately equal increase in the yield of formic acid, which rises from 0.3 to 120 millimoles per 100 millimoles of glucose dissimilated in the *A. aerogenes* fermentation.

Introduction

Fermentation of carbohydrates by the 2,3-butanediol producing bacteria always yields some organic acids that will inhibit the growth of the organism if allowed to accumulate. To obtain complete fermentation of reasonably large amounts of carbohydrates, i.e., 3% or more, it is necessary to neutralize these acids as they are formed. This is usually accomplished by addition of an excess of calcium carbonate to the medium, which maintains the pH reasonably constant in the range 5.6 to 5.8.

Buffers such as phosphates are not practicable because such large amounts are involved that their concentration has to be too high. Consequently, studies of the effect of pH on the butanediol fermentation have been made by adding a strong base, such as sodium hydroxide, manually from time to time to keep the hydrogen ion concentration within a certain range. In this way, Mickelson and Werkman (9) were able to show that fermentation of glucose by *Aerobacter indologenes* gave more formic and acetic acids and less butanediol when the fermentations were run above pH 6.3 than when they were run in more acidic solutions. A similar effect has been observed with *Bacillus polymyxa* (1) and *Bacillus subtilis* (12). In these experiments, close control of the pH was not possible, and it may have varied by as much as

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2 pH units. The present paper describes results in which the pH was controlled within ± 0.05 pH units, by using an electronic pH monitor giving automatic control (3).

Although close control of the hydrogen ion concentration has not been tried previously on butanediol fermentations as far as the authors know, laboratory apparatus for automatic pH control of bacterial fermentations has been used before. Longworth and McInnes (6, 7, 8) have devised an apparatus giving automatic control of pH of bacterial fermentations and have studied the rate of formation of acids by *Lactobacillus acidophilus*. A similar apparatus has recently been described by Kepes (5).

Experimental

Organisms Used

Bacillus polymyxa, Strain No. C-2(1). This strain was isolated from soil in the Ottawa laboratories of the National Research Council.

Bacillus subtilis (Ford's Type) Strain No. 44, used in previous work (2).

Serratia marcescens, Strain No. S 16. This was obtained from Prof. B. Eagles at the University of British Columbia where it was designated as *Serratia F. V.*

Aerobacter aerogenes, Strain M 148. This was isolated from soil at the Ottawa laboratories of the National Research Council.

Preparation of Inoculum and Medium

The inoculum was prepared by transferring the organism from an agar slant into 10 ml. of a medium containing glucose (1%) and yeast extract (0.5%). It was then incubated for 24 hr. at the temperature to be used in the experiment. The fermentation medium contained glucose (5%), yeast extract (0.5%), potassium dihydrogen phosphate (0.05%), potassium monohydrogen phosphate (0.05%), and magnesium sulphate (0.02%). Each fermentation was run using 250 ml. of medium in a modified 1 liter Erlenmeyer flask (described below). The glucose (12.500 gm.) was autoclaved with 150 ml. of distilled water in the fermentation flask; the yeast extract and salts were sterilized separately, each in 50 ml. of distilled water. These solutions were added aseptically to the fermentation flask after cooling to room temperature. The purest grades of glucose and salts commercially available were used; the yeast extract was a Difco preparation.

Fermentation Apparatus

The electronic pH monitor, shaking apparatus, and the metering pump have been previously described by the inventors (3). The monitor was found to be quite reliable and it fills a long-felt need for a rugged, accurate, and dependable apparatus for laboratory control of the pH of fermenting solutions.

The fermentation flask and electrodes used in this investigation are shown in Fig. 1. The flask is a modified 1 liter Erlenmeyer provided with gas inlet (*A*) and outlet (*B*) tubes, an alkali inlet (*E*), an inoculum inlet (*F*) and two standard taper joints for insertion of the electrodes. The glass electrode (*D*) is a Leeds and Northrup Std. 1199-12 and is mounted in a standard taper 24/40 joint by a rubber tube connection as shown in Fig. 1. The calomel electrode and potassium chloride bridge are Leeds and Northrup Std. 1199-23-A and Std. 1199-27-A respectively. The reservoir is removed from the potassium chloride bridge and the 12 mm. diam. Pyrex tube containing the porous ring seal is fused to a standard taper 24/40 joint to give the calomel electrode assembly (*C*) shown in Fig. 1. The glass electrode and salt bridges are all of the same length from the top of the ground joint downwards (172 ± 2 mm.), so they are interchangeable, from one flask to another. The train used for purifying the gases and for the adsorption of the fermentation gases is similar to that previously used (10). Temperature control was achieved within ± 0.2 degrees Centigrade by placing the fermentation shaker in a constant temperature room.* The monitor, as well as the trains for purifying and absorbing the gases, was outside this room. The electrode leads and gas inlet and outlet tubes passed through holes in the wall.

Sterilization of the Electrodes and Accessory Equipment

In early work, the electrodes were sterilized chemically with mercuric chloride or hydrochloric acid and then washed in sterile distilled water. This rather lengthy procedure has been replaced by the use of germicidal light. The electrodes are now sterilized in the apparatus shown in Fig. 2. This is

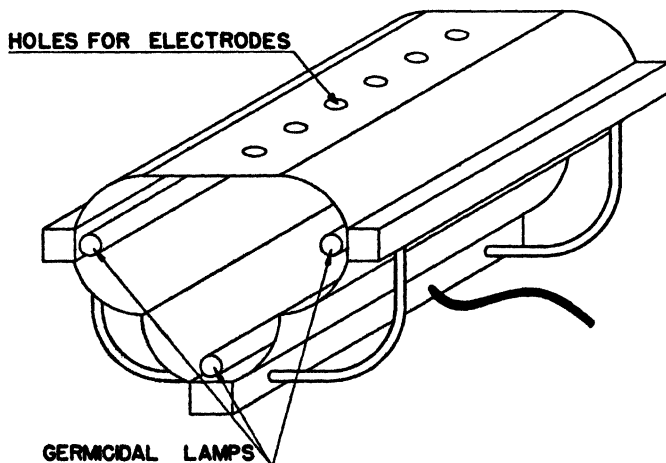


FIG. 2. Apparatus for sterilizing electrodes by ultraviolet light.

an aluminum box with three 18 in. germicidal lights mounted, one on each side and one on the bottom. The holes in the top are adjusted so a 24/40 S.T. joint is arrested after entering the hole about half way. The electrodes

* An early model of the shaker not having built-in temperature control was used in these studies.

PLATE I

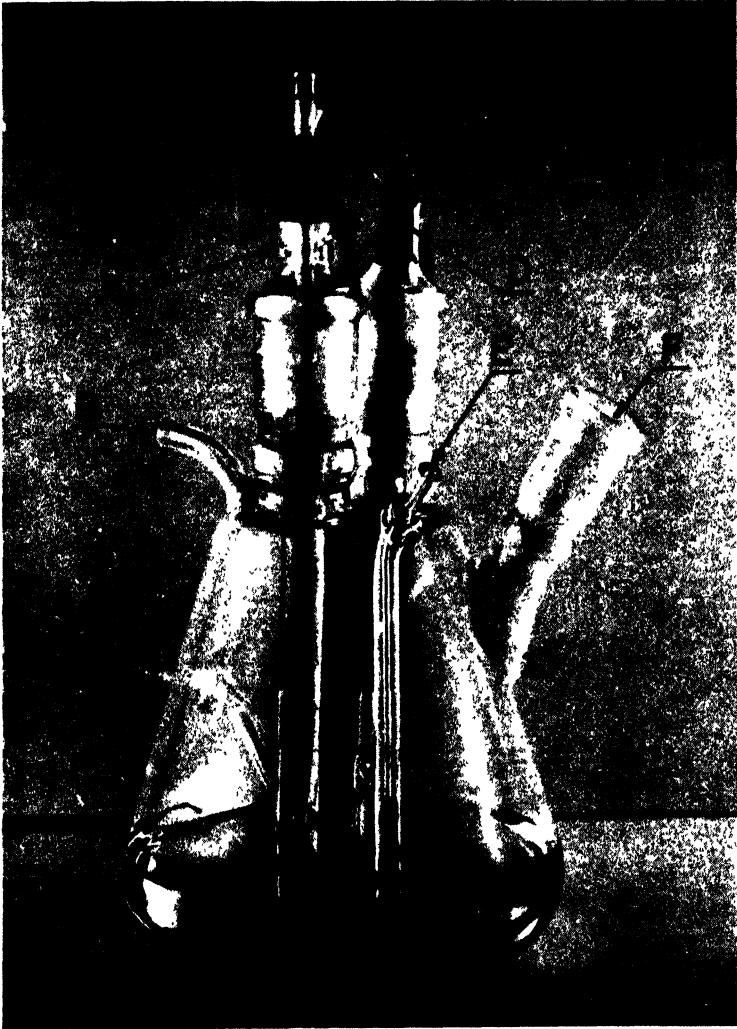


FIG. 1. *Flask and electrodes used in studies of pH controlled fermentations.*

are removed from the distilled water, in which they are usually stored, and inserted in these holes. After an irradiation period of 10 min. they are rotated through 90 degrees and then after 10 min. more they are removed and inserted quickly into the fermentation flask. This treatment has been found to sterilize electrodes that have been immersed in a thick sporulating suspension of *Bacillus subtilis*. The burettes used as alkali reservoirs with their connecting tubes are sterilized in the autoclave. The alkali is prepared by diluting concentrated ammonium hydroxide with sterile water.

Procedure for Starting the Fermentations

The inoculum, sterile medium, and sterile alkali are prepared the day before the fermentation is to be started and the potential of the electrodes measured in a buffer at the pH and temperature to be used in the experiment in order to obtain the correct potentiometer settings. The electrodes are sterilized by ultraviolet light as described above and transferred quickly to the fermentation flasks, which are placed directly in front of the sterilizer. The ground glass joints are then raised slightly and daubed with sterile grease to ensure a gas-tight connection. The flasks are then placed in the shaker of the fermentation apparatus and the electrodes and the gas inlet and outlet tubes are connected to the rest of the system. The alkali inlet tubes are then connected, care being taken first, to displace the air from the rubber tube by drawing off 10 ml. of alkali. The medium is allowed to shake for about half an hour until its temperature reaches that of the incubator and the pH then adjusted to the desired value by addition of sterile ammonium hydroxide through the pump, or of sterile hydrochloric acid (2 *N*) from a medicine dropper through the inoculum inlet. The strength of the ammonium hydroxide solution used is governed by the pH of the fermentation. Large amounts are required for fermentations run at pH's above 7, and 4 *N* base is usually used. For pH's between 6 and 7, 2 *N* base is employed, while for fermentations below pH 6, 1 *N* base is preferable.

While the pH is being adjusted, the metering pumps are also adjusted to deliver approximately 0.3 ml. per min. The inoculum then is poured aseptically into the fermentation flask through the neck provided for that purpose. The final adjustment of the pH is now made and the inoculum inlet is closed by means of a ground-glass stopper treated with sterile grease to give a gas-tight seal. The alkali burettes are now filled. These burettes are read from time to time during the fermentations in order to follow the rate of acid formation. Variations of the pH of the medium are recorded by a recording milliammeter connected to the pH monitor. When the fermentation is finished, acid production stops owing to disappearance of the glucose, and the medium usually becomes alkaline, possibly because of the action of amino acid decarboxylases. One or two hours is allowed, to make sure the fermentation gases have been swept out, the new balance point is measured, and a 50 ml. sample of the medium is then taken and its pH measured on an independent instrument. This is done to make sure

there has been no drifting of the potential of the electrodes in the fermentation flask. A small sample is taken for bacteriological examination at this stage. Repeated tests have failed to show the presence of any contaminants. The electrodes are removed from the fermentation flask and replaced with rubber stoppers. The 50 ml. sample is returned to the fermentation flask quantitatively and a 50% excess of 5 *N* hydrochloric acid poured from a graduated cylinder through the inoculum inlet, which is quickly stoppered, and the medium then swept out for a period of three hours or more, with shaking to remove the dissolved carbon dioxide formed by decomposition of carbonates. The electrodes are washed by dipping them several times in distilled water; they are then stored in distilled water.

Analysis of Fermented Solutions

The fermented solution is mixed with the contents of the cold trap and then cleared with zinc hydroxide as described previously (10), the only difference being that the solutions are now made up to 500 ml. The analyses are conducted as before, except for improvements in the determination of the acids and the carbon assimilated. The acids are now determined by a method based on partition chromatography (11). The carbon assimilated is determined using the manometric method of Van Slyke and Folch (13). This determination is made on a fraction representing the carbon precipitated by zinc hydroxide plus the carbon in nonvolatile compounds *not* extracted by ether from neutral or acidic aqueous solutions. This fraction is obtained by combining the thrice-washed zinc hydroxide precipitate with an equivalent amount of the aqueous solution obtained after extraction of the neutral products and acids by ether. A fraction representing one-tenth of the total fermentation solution is made up to 200 ml. and a 5 ml. aliquot of the thoroughly mixed suspension is pipetted into the combustion tube. It is then dried in a vacuum desiccator and analyzed by the macro method (13). The carbon found is corrected for any glycerol or residual sugar in the fermented solution. A blank determination is made on a solution containing the same amount of yeast extract as the fermentation medium. When further corrected for this blank the carbon is taken to be the glucose carbon assimilated by the micro-organisms, since all the fermentation products, except glycerol, are either extracted by ether or volatilized.

Results and Discussion

Carbon balances showing the effect of variation of pH on the anaerobic dissimilation of glucose by *B. polymyxa*, *A. aerogenes*, *S. marcescens*, and *B. subtilis* are shown in Tables I, II, III, and IV respectively. Because of the similarity of the results obtained, these tables will be considered collectively.

The over-all rate of glucose dissimilation at the optimum hydrogen ion concentration is some three to six times as fast as that previously found with these organisms in calcium carbonate buffered media. It was found that the

TABLE I

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Bacillus polymyxa*

All fermentations were incubated at 30° C. using a medium containing 5.0% glucose and 0.5% yeast extract. The pH was controlled by automatic addition of ammonium hydroxide while anaerobic conditions were maintained by bubbling purified nitrogen through the medium.

Product	pH 5.40	pH 5.80	pH 6.20	pH 6.47	pH 6.80	pH 7.17	pH 7.60
	Millimoles per 100 millimoles of glucose dissimilated						
2,3-Butanediol	43.3	51.3	50.5	49.7	44.2	33.2	11.3
Acetoin	2.32	1.77	2.36	1.88	3.48	2.88	4.90
Ethanol	67.4	71.4	73.1	69.3	67.3	75.0	78.9
Glycerol	2.90	3.39	2.84	2.24	3.23	2.02	2.39
Acetone	2.23	0.34	0.38	0.21	Nil	0.33	Nil
Butyric acid	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Acetic acid	1.85	2.11	3.15	6.32	16.59	26.45	46.7
Formic acid	0.47	0.22	2.76	1.61	3.56	4.81	82.6
Succinic acid	1.68	0.79	0.64	0.21	1.67	6.65	4.45
Lactic acid	0.75	1.67	2.12	1.67	1.84	3.20	6.52
Carbon dioxide	183.9	186.5	183.1	187.1	175.3	161.2	78.9
Hydrogen	89.2	68.0	70.4	78.0	84.1	82.1	46.0
Glucose carbon assimilated	32.8	—	—	—	31.9	—	29.6
Fermentation time, hr.	53	30	26	26	26	28	53
% glucose used*	99.6	100.0	100.0	100.0	100.0	99.9	9.44
% carbon accounted for	93.9	94.1	94.8	93.5	98.8	95.0	91.6
O/R index	1.01	1.00	0.97	1.01	0.99	0.98	0.99

* Determined by direct estimation of the glucose before and after fermentation.

TABLE II

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Aerobacter aerogenes*

Fermentations run under the same conditions as for *B. polymyxa* (Table I)

Product	pH 5.00*	pH 5.00	pH 5.20	pH 5.60	pH 6.00	pH 6.60	pH 7.00	pH 7.60	pH 8.00
	Millimoles per 100 millimoles of glucose dissimilated								
2,3-Butanediol	40.2	38.7	48.8	47.9	47.5	38.8	10.78	Nil	Nil
Acetoin	2.43	2.46	1.39	2.39	1.58	2.10	3.08	3.85	5.82
Ethanol	56.4	60.5	61.2	56.3	57.4	55.2	57.7	54.7	60.9
Glycerol	4.13	2.22	1.81	3.91	3.34	4.37	5.79	7.72	6.55
Acetone	Nil	Nil	0.53	Nil	0.07	Nil	Nil	Nil	Nil
Butyric acid	1.07	0.59	0.29	0.07	Nil	0.44	0.68	1.79	3.95
Acetic acid	23.7	20.8	3.89	4.23	7.96	12.95	42.3	52.7	52.6
Formic acid	0.50	0.26	0.43	0.36	0.77	0.44	22.5	52.4	119.6
Succinic acid	1.25	1.29	2.17	2.04	1.80	3.08	6.19	4.10	9.29
Lactic acid	3.15	3.49	2.34	2.64	3.35	7.59	25.0	36.5	9.80
Carbon dioxide	188.0	190.5	183.8	171.1	174.0	167.0	106.8	77.4	19.60
Hydrogen	98.9	103.0	69.8	57.6	74.2	80.7	81.4	69.7	10.37
Glucose carbon assimilated	—	37.6	42.5	66.2	65.1	93.0	87.6	53.2	83.1
Fermentation time, hr.	143	142	94	29½	14½	10½	10	9½	21
% glucose used	65.5	68.0	99.9	100.0	100.0	100.0	100.0	99.9	93.4
% carbon accounted for	91.1	96.9	97.0	97.9	99.0	101.8	98.6	94.9	95.9
O/R index	1.10	1.10	1.07	1.06	1.03	1.06	1.00	1.07	1.07

* Duplicate runs were made at pH 5.00 because the sudden increase in acetic acid and hydrogen was unexpected and needed confirmation.

TABLE III

ANAEROBIC DISSIMILATION OF GLUCOSE BY *Serratia marcescens*Fermentations run under the same conditions as for *B. polymyxa* (Table I)

Products	pH 6.40	pH 6.80	pH 7.20	pH 7.60	pH 7.80
	Millimoles per 100 millimoles of glucose dissimilated				
2,3-Butanediol	55.2	49.4	30.1	2.48	Nil
Acetoin	1.58	1.87	3.99	6.21	5.87
Ethanol	46.7	49.9	49.5	49.3	41.0
Glycerol	2.16	6.78	2.79	2.44	9.61
Acetone	Nil	0.13	Nil	Nil	Nil
Butyric acid	Nil	0.24	Nil	1.49	1.49
Acetic acid	1.90	6.32	28.2	51.8	49.0
Formic acid	45.7	59.2	85.6	113.5	91.4
Succinic acid	2.86	4.35	7.52	5.81	4.75
Lactic acid	9.66	8.81	18.21	61.6	64.8
Carbon dioxide	116.1	106.5	53.1	2.76	2.16
Hydrogen	0.78	0.16	0.49	1.81	0.15
Glucose carbon assimilated	63.9	46.6	59.1	61.5	38.1
Fermentation time, hr.	94	31	21	34	40
% glucose used	94.9	100.0	99.9	100.0	99.9
% carbon accounted for	99.4	98.8	97.1	102.5	98.0
O/R index	1.06	1.07	0.99	1.06	0.95

TABLE IV

ANAEROBIC DISSIMILATION OF GLUCOSE BY *B. subtilis* (FORD'S TYPE)

Products	pH 6.00	pH 6.20	pH 6.40	pH 6.60	pH 6.80	pH 7.20	pH 7.60	pH 8.00
	Millimoles per 100 millimoles of glucose dissimilated							
2,3-Butanediol	36.8	39.5	32.3	27.7	20.8	17.65	11.82	Nil
Acetoin	1.31	2.65	0.99	2.89	2.37	1.44	2.99	2.10
Ethanol	20.51	15.05	13.81	15.10	20.2	20.4	22.3	36.9
Glycerol	29.9	31.1	33.5	19.81	18.99	12.61	10.32	17.00
Butyric acid	0.17	0.32	0.46	0.86	0.98	0.89	2.38	1.30
Acetic acid	0.87	1.16	0.74	2.24	2.36	7.44	12.81	49.5
Formic acid	12.38	16.57	11.52	19.00	17.63	27.6	39.6	96.0
Succinic acid	1.08	0.73	0.82	0.98	1.12	0.89	2.24	4.56
Lactic acid	41.4	65.6	70.9	97.1	95.0	106.7	119.0	54.1
Carbon dioxide	91.4	86.4	80.6	60.2	59.6	40.0	32.4	3.47
Hydrogen	0.38	0.48	0.16	1.81	0.49	0.23	0.33	0.78
Glucose carbon assimilated	82.1	15.8	15.2	33.4	28.4	25.3	22.6	21.2
Fermentation time, hr.	71	87	62	31	32	22	23	47
% glucose used	85.2	97.9	100.0	100.0	100.0	100.0	100.0	94.7
% carbon accounted for	100.0	102.0	98.0	104.3	100.3	98.3	105.0	92.8
O/R index	1.06	1.08	1.08	0.98	1.07	0.98	1.05	1.09

optimum rate of glucose dissimilation occurred in neutral or slightly alkaline media (see Fig. 3). It is interesting to note that these bacteria vary considerably in their sensitivity to changes in pH. The rate of glucose dissimilation by *A. aerogenes* and *B. polymyxa* is nearly constant over quite a

wide pH range, while the other two species have a rather sharp optimum due chiefly to their inhibition in acid solutions. The increased rate obtained at a favorable hydrogen ion concentration is partly due to an increased population

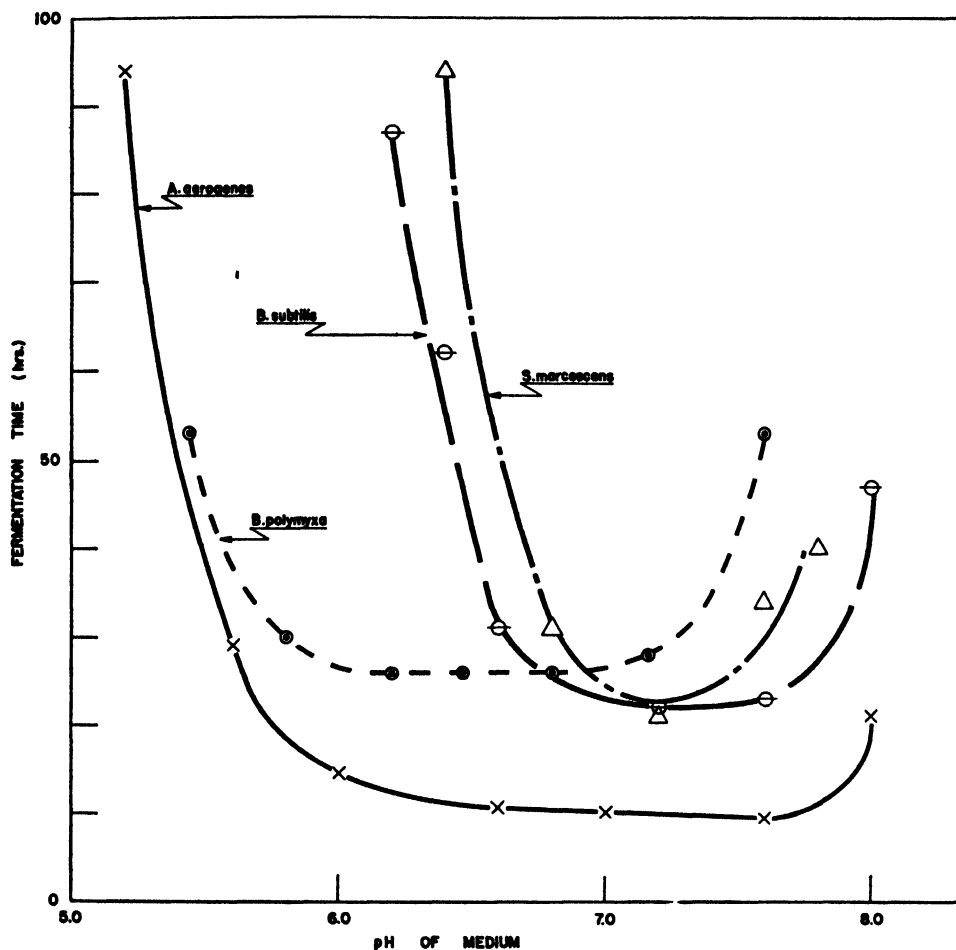


FIG. 3. Effect of pH on rate of dissimilation of glucose. The fermentation time is that required for complete fermentation of the glucose (5% concentration).

of bacteria. Accurate counts of the numbers of bacteria per unit volume were not made, but mere visual inspection of the turbidity shows that at the optimum pH greatly increased growth is obtained. Longworth and MacInnes (8) found that *Lactobacillus acidophilus* gave a fourfold increase in growth and a ninefold increase in acid production when grown at pH 6.0, compared to the increase in a culture grown without control of the acidity. It would be interesting to study the effect of pH on the kinetics of sugar breakdown by the 2,3-butanediol bacteria, and to relate the rate of fermentation with the numbers of viable and total cells.

Variation of the hydrogen ion concentration caused a marked variation in the relative yields of products. This is especially striking with 2,3-butanediol, the yield decreasing markedly above pH 6.4, until above pH 7.6 little or

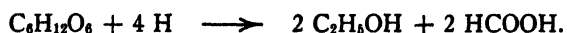
none is formed. At the same time the acetoin tends to increase. It must be remembered that these figures are relative yields, and one reason for the decrease of 2,3-butanediol is failure for its production to increase as rapidly as that of other products, such as lactic acid, when the pH is increased. For example, *A. aerogenes* is producing 2,3-butanediol at approximately twice as fast an absolute rate at pH 7.0 when 10.8 millimoles are produced in 10 hr. as at pH 5.2 when 49 millimoles are produced in 94 hr., yet the relative yield at pH 7.0 is less than one-quarter that at pH 5.2. If a homo-fermentative strain, forming 2,3-butanediol, could be obtained it might give its best fermentation at about pH 7.0.

In general the acids are formed in greatest amounts in alkaline media. Lactic acid is formed in optimum yield at pH 7.6. The yield of acetic acid passes through a minimum at pH 5.2 with *A. aerogenes* (see table II), more than five times as much being made at pH 5.0, but the best yields are obtained above pH 7.0. It was not possible to demonstrate this minimum with the other organisms, since they do not ferment rapidly enough at pH 5.0 to make the experiments practicable.

One of the most striking changes is the large increase in formic acid formation that occurs with *B. polymyxa* and *A. aerogenes*. These organisms produce only traces of this acid in acidic media but it is one of the major products in alkaline media. For example *A. aerogenes* produces almost 120 millimoles for every 100 millimoles of glucose fermented at pH 8.0, while at pH 5.0 to 6.6 less than 0.5 millimole is formed. Concomitant with this large increase in formic acid there is an almost equally large decrease in the yields of carbon dioxide and hydrogen. This suggests that these organisms normally produce hydrogen in acidic media by enzymic decomposition of formic acid but when they are grown in alkaline media formic acid accumulates owing to inhibition of this reaction. Even with the other organisms that never produce much hydrogen (Tables III and IV) there is an increase in the amount of formic acid in alkaline media, while the production of carbon dioxide may fall to only 2 to 3 millimoles for each 100 millimoles of glucose dissimilated. This decrease is partly due to increase in the lactic acid fermentation, which does not yield carbon dioxide, and is partly due to the accumulation of formic acid. In general, these four species can all be considered to carry out the following over-all reaction in alkaline medium.



The four hydrogen atoms produced in this reaction could then be used to produce more formic acid by other reactions such as:



The carbon balances in this paper are in agreement with this hypothesis. It is difficult to explain why formic acid should be obtained by several different reactions unless the enzyme systems or carriers responsible for eliminating carbon dioxide from the cell are functioning at a greatly reduced rate.

Succinic and butyric acids, though never produced in very large amounts, show an increased yield in alkaline media. The yield of ethanol is not affected much by variation in the hydrogen ion concentration. The yield of glycerol is changed somewhat and seems to pass through a minimum at pH 7.6 (see Table IV).

To obtain good carbon recoveries it is necessary to determine the carbon assimilated, since as much as 15% of the glucose carbon may be found in this fraction. It will be noted that the redox balances are usually somewhat in excess of the theoretical value of 1.00. This is to be expected since the glucose carbon assimilated must be partly synthesized to compounds such as fats and protein, which are more reduced than glucose, yet these were not considered in working out the redox balance owing to uncertainty regarding the magnitude of the negative value to use in calculating their contribution.

Although the results of this investigation have been discussed in terms of the effect of variation of the hydrogen ion concentration on the rate of the fermentations and yields of products, it must be remembered that hydrogen ions may have an indirect effect. These changes may be caused by variation in the amounts of undissociated organic acids (8), ammonium ions, or undissociated ammonium hydroxide, since these vary in concentration as the hydrogen ion concentration is varied. Furthermore, whatever the causative agent may be, it need not act directly on the enzymes of mature cells but may affect growing cells in such a way that production of certain enzymes is inhibited. The latter effect has been demonstrated by Brewer, Mickelson, and Werkman (4) for *Aerobacter indologenes*. They found that the nature of the enzymic activity of nonproliferating cells on glucose in both acid and alkaline buffers depends on the nature of the medium in which the cells are grown. Cells grown in acid glucose media produced more 2,3-butanediol than cells grown in alkaline media whether tested in acid or alkaline glucose solution although more was produced in the acid test media. However, although the best yield of formic acid was obtained in an alkaline glucose solution, it was obtained using cells originally grown in an acid glucose medium. Hence this type of adaptation will not completely explain the results of the present investigations: it is necessary also to postulate an effect on the fermentation apparatus of mature cells.

Since hydrogen ions enter into many biological oxidation-reduction reactions one can expect the redox potential to depend on the pH of the medium. Although it is not yet certain what the apparent redox potential of a fermentation signifies it should be very instructive to examine the relation between pH and eH with the 2,3-butanediol bacteria.

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POLYVINYL NITRATE¹

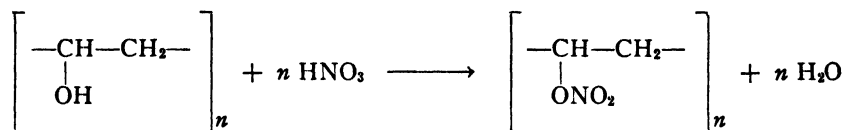
BY S. A. V. DEANS² AND R. V. V. NICHOLLS

Abstract

Existing methods of nitration of polyvinyl alcohol involving the use of fuming nitric acid alone, or mixtures of fuming nitric acid and sulphuric acid, have been modified to give products improved in nitrogen content, color, and yield. A method involving the use of fuming nitric acid and acetic anhydride has been developed. The explosive characteristics of polyvinyl nitrate of various degrees of polymerization prepared by five different methods are reported.

Introduction

The hydroxyl groups in polyvinyl alcohol tend to react in the same manner as the hydroxyl groups present in simple alcohols. In particular they are capable of being esterified to form polyvinyl esters. Organic esters of polyvinyl alcohol are well known but the nitrate is the only inorganic ester of polyvinyl alcohol that has been prepared:



In general, esters of nitric acid, such as the alkyl nitrates, nitroglycerine, nitrostarch, and nitrocellulose, possess explosive properties. Polyvinyl nitrate is no exception.

Frank and Kruger (5) found that the methods of nitration customarily employed for glycerol, starch, and cellulose were not applicable to polyvinyl alcohol. In order to reduce the tendency for oxidation to occur, they dissolved the polyvinyl alcohol in sulphuric acid and added the solution to a nitrating mixture containing excess sulphuric acid. Polyvinyl nitrate was obtained in the form of pale yellow plastic granules, the yield being 80%. The product contained 10% nitrogen, the maximum theoretical value being 15.7%. It could be detonated either by heat or shock.

Burrows and Filbert (2, 3) showed that finely powdered polyvinyl alcohol tended to float on the surface of fuming nitric acid where it would ignite and continue to burn in contact with the air. When the polyvinyl alcohol was finally immersed in the nitrating acid, the reaction was so rapid that the material was largely oxidized. To avoid this side reaction, the powdered polyvinyl alcohol was first mixed with enough water to render it moist and

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cohesive. It was then grained through a 30 mesh screen and dried. It was found that this grained material could be more readily immersed beneath the surface of the nitrating acid, and thus the tendency for oxidation to occur was reduced to a minimum. The temperature was maintained at 15° to 20° C. and the syrupy orange-red solution thus obtained was poured into cold water, the polyvinyl nitrate precipitating as a cream-colored powder in 80% yield. The product contained 13.8% nitrogen, the maximum theoretical value being 15.7%. With less concentrated nitric acid, the polyvinyl nitrate was obtained in smaller yield and the product possessed a lower nitrogen content.

In the present investigation a detailed study of the preparation of polyvinyl nitrate was carried out. The addition of powdered polyvinyl alcohol to fuming nitric acid alone, to fuming nitric acid – acetic anhydride mixtures, and to fuming nitric acid – fuming sulphuric acid mixtures gave rise to polyvinyl nitrate. Furthermore, the addition of an acetic anhydride suspension of polyvinyl alcohol to fuming nitric acid – acetic anhydride mixtures and to fuming nitric acid – fuming sulphuric acid mixtures also gave rise to polyvinyl nitrate. These five methods were applied to polyvinyl alcohol of various degrees of polymerization.

The tests on polyvinyl nitrates of various degrees of polymerization as obtained by these five different methods of preparation included the softening point, the Trauzl lead block test, the impact test, the ignition test, and the Abel heat test.

Experimental Procedures

1. PREPARATION OF POLYVINYL ALCOHOLS

Polyvinyl acetates of various degrees of polymerization were obtained from Shawinigan Chemicals Ltd.*, Shawinigan Falls, Que., and were converted into polyvinyl alcohols. The yields and residual-acetate contents are presented in Table I. The polyvinyl alcohol was prepared by adding a methanolic

TABLE I
CONVERSION OF POLYVINYL ACETATE INTO POLYVINYL ALCOHOL

Polyvinyl acetate Average degree of polymerization (No. of structural units)	Polyvinyl alcohol	
	Yield, %	Residual acetate, mole %
30	87.3	0.60
70	93.2	0.63
150	93.8	0.89
230	93.8	1.21
350	95.4	1.47
700	97.7	1.68

We wish to acknowledge several donations of generous samples of these polymers.

solution of polyvinyl acetate to a dilute methanolic solution of sodium methoxide.* It will be observed that the yield and residual acetate content of the polyvinyl alcohol increased with an increase in the degree of polymerization of the polyvinyl acetate from which it was formed.

The polyvinyl alcohols were converted into polyvinyl nitrates by a variety of methods. The original intention was to observe the effect of variation in the chain length on the explosive characteristics of the polyvinyl nitrate.

2. PREPARATION OF POLYVINYL NITRATES

1. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid*

In a 500 cc. round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a small solids funnel was placed 200 cc. of fuming nitric acid (95%). Exactly 15 gm. of polyvinyl alcohol, reduced to a fine powder by means of a ball mill, was added through the funnel in small portions over a period of 30 min. with efficient stirring, the reaction mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the yellow solution was poured into a well stirred mixture of 1000 gm. of ice and water in order to precipitate the polyvinyl nitrate.

In the case of polyvinyl alcohols of very high degree of polymerization it was found advantageous to employ somewhat larger amounts of fuming nitric acid since the viscosity of the resultant solution was high.

It should be noted that by carrying out the nitration at -10° to -5° C. there was no tendency for powdered polyvinyl alcohol to ignite even though it floated on the surface of the nitrating acid in contact with the air for several seconds.

The form of the product depends on its degree of polymerization. Polyvinyl nitrates of low degree of polymerization precipitated in the form of a white powder. Polyvinyl nitrates of high degree of polymerization, on the other hand, tended to coagulate in the form of tough white strands, thus giving rise to a bulky material. In either case, the mixture was filtered with suction and the product washed with water until the filtrate was neutral to litmus.

The purification of polyvinyl nitrate could be effected in a satisfactory manner only when the product was obtained in the form of a powder. In order to remove any impurities occluded by the small particles of polyvinyl nitrate, the latter was ground in a ball mill in the presence of 300 cc. of water for a period of 12 hr. The suspension of polyvinyl nitrate thus obtained was filtered with suction and the product washed with water until free of acid. The purification procedure was repeated to ensure complete removal of impurities. The product was then dried by exposure to the air.

On the other hand, when polyvinyl nitrate was obtained in a bulky form, it could not be ground in the ball mill and was therefore allowed to soak in

* The use of sodium methoxide was recommended by Dr. D. McIntosh, Shawinigan Chemicals Ltd., Shawinigan Falls, Quebec.

water for a period of two days after which it was filtered and allowed to dry by exposure to the air.

2. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid - Acetic Anhydride Mixtures.*

In a 400 cc. beaker equipped with a mechanical stirrer and a thermometer was placed 100 cc. of technical acetic anhydride. The beaker was maintained at a temperature of -10° to -5° C. and 100 cc. of fuming nitric acid (95%) was slowly added. Exactly 15 gm. of polyvinyl alcohol, reduced to a powder by means of a ball mill, was added to small portions over a period of 30 min. with efficient stirring, the reaction mixture being maintained at -10° to -5° C. throughout the experiment. The polyvinyl nitrate was thus obtained as a fine suspension in the nitrating acid. Stirring was continued for another hour in order to complete the nitration.

It was possible to obtain the polyvinyl nitrate by filtration but the product tended to coagulate, thus forming an elastic mass that could not be readily purified. Instead, therefore, the suspension of polyvinyl nitrate was poured into a well stirred mixture of 1000 gm. of ice and water, thus precipitating the polyvinyl nitrate in the form of a white powder. The mixture was filtered with suction and the product washed until free of acid. It was then purified by grinding in a ball mill in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and drying by exposure to the air.

The present method was most suitable for polyvinyl alcohols of high degree of polymerization. In the case of polyvinyl alcohols of low degree of polymerization (below 150), however, the product, in suspension in the nitrating acid, tended to coagulate even when the stirring was very efficient, thus forming an elastic mass that could not be readily purified. It was possible to avoid this difficulty by using a larger quantity of nitrating acid but in the case of polyvinyl alcohols of very low degree of polymerization (e.g., 30) the product tended to coagulate as rapidly as it was formed.

Using fuming nitric acid - acetic anhydride mixtures, unlike the use of fuming nitric acid alone, there was no tendency for the polyvinyl alcohol to ignite on the surface of the nitrating acid even at room temperature. It was necessary to carry out the reaction at -10° to -5° C., however, since the tendency for the product to coagulate in the nitrating acid increases markedly above this temperature.

3. *By Adding Powdered Polyvinyl Alcohol to Fuming Nitric Acid - Fuming Sulphuric Acid Mixtures.*

In a 400 cc. beaker equipped with a mechanical stirrer and a thermometer was placed 100 cc. of fuming nitric acid (95%). The beaker was maintained at -10° to -5° C. and 100 cc. of fuming sulphuric acid (free sulphur trioxide about 20%) was slowly added. Exactly 15 gm. of polyvinyl alcohol, reduced to a powder by means of a ball mill, was added in small portions from a spatula over a period of 30 min. with efficient stirring, the reaction mixture

being maintained at -10° to -5° C. throughout the experiment. The polyvinyl nitrate was obtained as a suspension in the nitrating acid. Stirring was continued another hour in order to complete the nitration.

As in the previous method of nitration, it was possible to obtain the polyvinyl nitrate by filtration of the suspension, but the product tended to coagulate to form an elastic mass that again could not be readily purified. Instead, therefore, the suspension of polyvinyl nitrate in nitrating acid was poured into a well stirred mixture of 1000 gm. of ice and water, the product precipitating in the form of a colored (buff to yellow) powder. The mixture was filtered by suction and the product washed until free of acid. It was purified by grinding it in a ball mill in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and drying by exposure to the air.

The present method, unlike previous ones, gave more colored products. A temperature of -10° to -5° C. was necessary since at higher temperatures the product tended to coagulate in the form of an elastic mass that then decomposed with liberation of brown fumes and deposition of a carbonaceous residue. It was effective for polyvinyl alcohols of high degree of polymerization only. In the case of polyvinyl alcohols of low degree of polymerization (below 230) the product, suspended in the nitrating acid, tended to coagulate even when the stirring was very efficient, thus forming an elastic mass that decomposed. It was possible to avoid this difficulty by using a larger quantity of nitrating acid but in the case of polyvinyl alcohols of very low degree of polymerization (e.g. 30) the product tended to coagulate and decompose as rapidly as it was formed.

4. By Adding an Acetic Anhydride Suspension of Polyvinyl Alcohol to Fuming Nitric Acid - Acetic Anhydride Mixtures

In a 1 liter round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a 500 ml. separatory funnel was placed 275 cc. of technical acetic anhydride. Then 275 cc. of fuming nitric acid (95%) was added with stirring at -10° C. A suspension of polyvinyl alcohol in acetic anhydride, prepared by grinding 50 gm. of polyvinyl alcohol in the presence of 300 cc. of technical acetic anhydride in a ball mill for 12 hr., was then added by means of a separatory funnel over a period of one hour with rapid stirring, the mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the suspension of polyvinyl nitrate thus obtained was immediately poured into 2000 gm. of ice and water with rapid stirring, the polyvinyl nitrate precipitating in the form of a white powder.

The mixture was filtered by suction and the product washed until free of acid. It was purified by grinding it in a ball mill in the presence of water to ensure complete removal of impurities and then drying the product by exposure to the air.

This method of preparation apparently may be applied to polyvinyl alcohols of any degree of polymerization, the product always being obtained in the form of a white powder. As in the method involving the addition of powdered polyvinyl alcohol to fuming nitric acid – acetic anhydride mixtures, there was no tendency for the polyvinyl alcohol to ignite on the surface of the nitrating acid even at room temperature. It was necessary to carry out the reaction at -10° to -5° C., however, since the tendency for the product to coagulate on the nitrating acid increased markedly above this temperature. Thus, for example, at 25° C., the polyvinyl nitrate coagulated in the form of an elastic mass on the stirrer almost immediately upon the addition of polyvinyl alcohol to the nitrating acid. On the other hand, at very low temperatures (-40° C.) the reaction rate was diminished and thus only a small yield of polyvinyl nitrate was obtained.

Alternatively, on adding an acetic anhydride suspension of polyvinyl alcohol to fuming nitric acid (95%) alone, the product at first tended to remain in solution in the nitrating acid but, on further addition of acetic anhydride suspension of polyvinyl alcohol, it precipitated in the form of an elastic mass that could not be readily purified.

5. *By adding an Acetic Anhydride Suspension of Polyvinyl Alcohol to Fuming Nitric Acid – Fuming Sulphuric Acid Mixtures*

In a 1 liter round-bottomed, three-necked flask fitted with a mechanical stirrer, a thermometer, and a 500 ml. separatory funnel was placed 300 cc. of fuming nitric acid. Then, 300 cc. of fuming sulphuric acid (free sulphur trioxide about 20%) was added slowly with stirring at -10° C. A suspension of polyvinyl alcohol in acetic anhydride, prepared by grinding 50 gm. of polyvinyl alcohol in the presence of 300 cc. of technical acetic anhydride in a ball mill for 12 hr., was then added by means of a separatory funnel over a period of one hour with rapid stirring, the mixture being maintained at -10° to -5° C. throughout the experiment. Stirring was continued for another hour and the suspension of polyvinyl nitrate thus obtained was immediately poured into 2000 gm. of ice and water with rapid stirring, the polyvinyl nitrate precipitating in the form of a colored powder.

The mixture was filtered with suction and the product washed till free of acid. It was then purified by grinding it in the presence of water for 12 hr., filtering, repeating the process to ensure complete removal of impurities, and then drying the product by exposure to the air.

This method of preparation may be applied to polyvinyl alcohols of any degree of polymerization, the product always being obtained in the form of a buff-colored powder. It was a poor method, however, since acetic anhydride and fuming sulphuric acid on mixing produced enough heat to cause decomposition of the product even when the stirring was very efficient and the mixture was maintained at -10° to -5° C.

3. PROPERTIES OF POLYVINYL NITRATE

In both the deacetylation of polyvinyl acetate to form polyvinyl alcohol and in the nitration of polyvinyl alcohol to form polyvinyl nitrate, fission of the polymeric chain may occur, thus giving rise to products of lower degree of polymerization than the original polyvinyl acetate. Throughout the discussion, however, it has been assumed for the sake of brevity that in a given preparation the degrees of polymerization of the polyvinyl acetate, polyvinyl alcohol, and polyvinyl nitrate are identical.

The nitrogen content of polyvinyl nitrate was determined by means of a Du Pont nitrometer (9, pp. 61-68). The nitrogen contents obtained for polyvinyl nitrate were in general between 13 and 15%, the maximum theoretical value being 15.73%.

The testing of polyvinyl nitrate as an explosive was carried out after the wetted samples had been dried at room temperature for a period of 36 hr. The actual tests* include softening point (1, p. 335), the Trauzl lead block test (8, pp. 104-106), the impact test, the ignition test, and the Abel heat test (6).

The softening point of polyvinyl nitrate was found to lie between 49 and 68° C. in all cases.

The Trauzl block values for polyvinyl nitrate varied from 153 to 341 cc. The value for standard trinitrotoluene obtained for purposes of comparison was found to be 255 cc.

In the impact test a small sample of polyvinyl nitrate was subjected to the shock of a falling weight (1780 gm.) in a Rotter Impact Machine, and the minimum height from which the weight had to fall in order to detonate the sample was noted. The value for standard trinitrotoluene, obtained for purposes of comparison, was 158 cm. The values obtained for polyvinyl nitrate varied from 30 to 335 cm. After these tests had been carried out, the samples were allowed to stand for a week. It was then found that the impact test gave much lower values, indicating increased sensitivity. This observation seemed to indicate that the polyvinyl nitrate was slowly decomposing.

The ignition test was performed by placing 0.02 gm. of polyvinyl nitrate in a test tube in a bath of Wood's metal at 100° C. and increasing the temperature at a rate of 20 degrees per minute until ignition occurred. The temperature at which brown fumes were evolved and the temperature at which ignition occurred were noted. The ignition point of polyvinyl nitrate in all cases was found to lie between 106° and 178° C.

The Abel heat test was carried out at 70° C. In all cases the values obtained were low as compared with, say, those of commercial cellulose nitrate with a heat test in excess of 10 min.

The properties of polyvinyl nitrate described above are set forth in detail in Tables II to VI.

* These tests were carried out by Mr. M. C. Fletcher, Chief Explosives Chemist, Department of Mines and Resources, Canada, whose assistance is acknowledged with gratitude.

TABLE II

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO FUMING NITRIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	89.0	14.8	—	341	86*	Nil	176	5	24
70	90.5	14.6	63	313	44	Nil	177	6	8
150	85.7	14.9	—	316	52	Nil	170	3	3
230	90.5	15.0	—	223†	36	164	170	1	10‡
350	93.0	14.9	—	211†	30	167	172	1	15‡
700	92.2	14.9	—	178†	30	173	178	1	23‡

* Value obtained for impact test six days later = 28 cm.

† Density of bulky polyvinyl nitrate as fired in lead block = 0.20 gm. per cc.

‡ Weight of bulky polyvinyl nitrate as used in Abel heat test = 1 gm.

TABLE III

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND ACETIC ANHYDRIDE

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
70	84.5	14.5	60	312	76	173	173	1	50
150	85.7	14.3	—	308	62	170	172	0	48
230	89.0	14.4	—	300	62	155	164	0	43
350	87.4	13.9	—	288	42	150	170	0	35
700	92.2	14.4	—	300	104	165	173	0	58

TABLE IV

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF POWDERED POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND FUMING SULPHURIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
70	88.5	14.2	59	280	44	122	122	1	48
150	89.0	14.9	—	230*	42	170	170	1	33
230	89.0	14.4	—	310	38	138	162	1	20
350	87.4	14.5	—	303	54	122	126	1	5
700	85.7	14.2	—	288	30	122	122	1	8

* The lead block test was carried out on 3.8 gm. of polyvinyl nitrate and calculated to 10 gm. basis.

TABLE V

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF ACETIC ANHYDRIDE SUSPENSION OF POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND ACETIC ANHYDRIDE

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	90.8	14.7	68	318*	335-Neg.	160	176	1	25
70	91.1	14.9	63	300	332	175	177	1	38
150	82.3	12.8	66	248	308	170	175	1	8
230	81.2	13.4	62	263	310	175	177	1	11
350	83.1	14.0	62	274	328†	165	168	1	20
700	86.0	13.8	66	153	335-Neg.	164	169	0	48

* Lead block test with No. 8 detonator = 298 cc.

† Impact test one week later = 32 cm.

TABLE VI

PROPERTIES OF POLYVINYL NITRATES PREPARED BY ADDITION OF ACETIC ANHYDRIDE SUSPENSION OF POLYVINYL ALCOHOL TO MIXTURE OF FUMING NITRIC ACID AND FUMING SULPHURIC ACID

Polyvinyl acetate Av. deg. of polym. (No. of struct. units)	Polyvinyl nitrate								
	Yield, %	N content, %	Softening point, °C.	Lead block expansion, cc.	Impact test, cm.	Ignition test		Abel heat test	
						Fumes, °C.	Ignition, °C.	Min.	Sec.
30	79.2	13.7	63	278	252	Nil	125	1	23
70	84.0	14.0	67	294	244	Nil	121	0	53
150	82.2	13.8	66	283	335*Neg.	Nil	138	2	45
230	82.6	13.7	64	265	335 Neg.	Nil	124	1	45
350	82.2	13.7	57	283	335 Neg.	Nil	120	1	27
700	81.2	13.5	49	286	335 Neg.	Nil	106	0	53

* Impact test one week later = 36 cm.

Discussion of Results

Previous workers have prepared polyvinyl nitrate by two methods. In the method employed by Frank and Kruger (5), in which a solution of polyvinyl alcohol in concentrated sulphuric acid was added to a cooled nitrating mixture containing excess sulphuric acid, the polyvinyl nitrate was obtained in 80% yield as a yellow-colored product containing only 10% nitrogen, the maximum theoretical value being 15.7%. The preliminary step, in which polyvinyl alcohol was dissolved in concentrated sulphuric acid, was considered necessary to avoid oxidation. In the present investigation it has been shown that powdered polyvinyl alcohol may be added directly to a mixture of fuming nitric acid – fuming sulphuric acid without any appreciable loss by oxidation

simply by carrying out the reaction at -10° to -5° C. The yields were somewhat higher (86 to 89%) and the nitrogen contents of the products (14.2 to 14.9%) were closer to the maximum theoretical value (15.7%).

In the method of Frank and Kruger the polyvinyl nitrate remained in solution in the nitrating acid (since a large excess was employed) but precipitated in the form of yellow-colored plastic granules on heating to 45° to 50° C. In the present method, however, in which a much smaller amount of nitrating acid was employed, the polyvinyl nitrate formed a suspension and was obtained as a colored powder simply by pouring it into ice and water with rapid stirring. It has also been found that polyvinyl nitrate may be prepared by adding an acetic anhydride suspension of polyvinyl alcohol to a mixture of fuming nitric acid and fuming sulphuric acid at -10° to -5° C. Again the product formed a suspension in the nitrating acid and was obtained as a buff-colored powder by pouring it into a mixture of ice and water with rapid stirring. This method likewise gave rise to colored products in 79 to 84% yield with nitrogen contents of 13.5 to 14.0%. This method suffers from the fact that much heat is produced on mixing acetic anhydride and sulphuric acid, thus causing oxidation of the product.

Burrows and Filbert (2, 3), on the other hand, preferred the use of fuming nitric acid alone at 15° to 20° C. in the preparation of polyvinyl nitrate. When powdered polyvinyl alcohol was added to fuming nitric acid at room temperature, it floated on the surface of the nitrating acid, where it tended to ignite and burn with a free flame, forming a carbonaceous residue. This tendency for oxidation to occur was largely avoided by Burrows and Filbert by graining the polyvinyl alcohol. This was accomplished by mixing the latter with sufficient water to render it moist and cohesive, passing it through a 30 mesh screen, and then drying. It was found that this grained material could be more readily immersed beneath the nitrating acid than powdered polyvinyl alcohol, thus reducing the tendency for oxidation to occur. The polyvinyl nitrate remained in solution in the nitrating acid and after stirring at 10° C. for some time the product was obtained in 80.3% yield in the form of a fine cream-colored product containing 13.8% nitrogen by pouring the solution into cold water. In the present investigation it was found that powdered polyvinyl alcohol could be added to fuming nitric acid without preliminary graining (i.e., conversion to particles of 30 mesh size) and without any tendency for the polyvinyl alcohol to burn on the surface of the nitrating acid simply by carrying out the reaction at -10° to -5° C. Polyvinyl nitrates of low degree of polymerization were obtained in the form of fine white powders and those of high degree of polymerization were obtained as a bulky material. The yields (86 to 93%), nitrogen contents (14.6 to 15.0%), and color (white) of the polyvinyl nitrates were better than those reported by Burrows and Filbert.

It has also been shown that polyvinyl alcohol may be nitrated by means of fuming nitric acid and acetic anhydride. In this case, powdered polyvinyl alcohol was added to the nitrating mixture at -10° to -5° C. and the resultant

suspension poured into ice and water, the product thus being obtained in 85 to 92% yield as a white powder containing 13.9 to 14.5% nitrogen.

Finally it was found that, when an acetic anhydride suspension of polyvinyl alcohol was added to a mixture of fuming nitric acid and acetic anhydride, the product was obtained in 81 to 91% yield as a white powder containing 12.8 to 14.9% nitrogen.

These five methods of preparation of polyvinyl nitrates were successfully applied to polyvinyl alcohols obtained from polyvinyl acetates having a degree of polymerization between 30 and 700. The products were generally obtained in the form of a powder, which was purified by grinding in a ball mill in the presence of water. The nitrogen content determined by means of the DuPont nitrometer in no case exceeded 15.0%, the maximum theoretical value being 15.73%. Other esterification reactions of polyvinyl alcohol such as acetylation and benzylation have likewise been found by Staudinger, Frey, and Starck (7) to give rise to incompletely esterified products.

The explosive characteristics of polyvinyl nitrate have not been reported in detail in the literature. Frank and Kruger (5) showed that polyvinyl nitrate may be detonated alone, or mixed with other explosives, either by shock or heat. In its sensitivity to shock and to friction and in its rate of burning it has been found to resemble nitrostarch (4).

In the present investigation it has been shown that polyvinyl nitrate is a very unstable substance, apparently decomposing at room temperature. The Trauzl lead block test indicated a high explosive power. The impact test, however, showed that the sensitivity of polyvinyl nitrate increases markedly when the compound stands at room temperature. The Abel heat test at 70° C. gave low values, indicating instability. The small percentage of carbonyl groups present in polyvinyl alcohol may be responsible in part for this instability. Polyvinyl nitrates cannot be recommended, therefore, as industrial or military explosives even for specialized uses.

Finally, polyvinyl nitrates obtained by all five methods of preparation showed little, if any, relation between explosive properties, nitrogen content, and degree of polymerization.

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SYNTHÈSE DES DÉRIVÉS ORGANOMAGNÉSIENS SANS ÉTHER¹

PAR ROGER BARRÉ ET JACQUES DE REPENTIGNY²

Sommaire

Les conditions d'obtention des dérivés organomagnésiens en l'absence d'éther ont été étudiées et précisées. Nous avons utilisé surtout les hydrocarbures aromatiques et l'éther de pétrole comme solvants, la diméthylaniline comme catalyseur ou support de la réaction. Dans le benzène, le toluène et le xylène, le rendement en iodure d'éthylmagnésium a été 80 à 82%, en bromure d'éthylmagnésium 86%. Les dérivés chlorure de *sec*-butylmagnésium, chlorure d'isoamyl magnésium et bromure de phénylmagnésium ont été préparés avec des rendements de 86, 80 et 81% respectivement; on n'a pu préparer le chlorure de *tert*-butylmagnésium. Les dérivés allyl et benzyl donnent de mauvais rendements. Le bromure d'éthylmagnésium et le chlorure de *n*-butylmagnésium ont été obtenus dans l'éther de pétrole avec des rendements de plus de 90%. Les temps de chauffage varient de 5 à 14 h. à 90° C.; la quantité de diméthylaniline varie suivant la nature des dérivés halogénés et les solvants; elle passe de 0.05 molécule-gramme à 1.25 molécule-gramme par molécule-gramme de dérivé halogéné. L'amine joue donc le rôle de catalyseur dans certaines réactions et de support de la réaction dans les autres. La méthode de dosage de ces dérivés Grignard est une modification de la méthode Gilman; pesée du magnésium résiduel et calcul d'après le magnésium consommé, décantation et dosage de l'hydroxyde de magnésium: ce qui donne deux chiffres de rendement. Cette modification permet d'évaluer l'importance des réactions secondaires par la différence de rendement entre les deux chiffres obtenus. Les dérivés Grignard préparés sans éther dans leur condensation avec quelques composés organiques se sont montrés aussi actifs que les dérivés obtenus dans l'éther.

Introduction

Nous avons pensé qu'il serait utile de répéter en les précisant davantage certaines expériences de préparation des dérivés Grignard sans éther. Il y a souvent avantage de pouvoir se servir dans cette réaction de solvants moins volatils que l'éther; ce solvant ne permet pas en effet de faire la condensation à une température élevée alors que souvent l'élévation de la température permet des réactions plus complètes, augmente les rendements et dans certains cas donne même une orientation nouvelle à la réaction. On peut faire la réaction dans l'éther d'abord puis enlever le solvant par distillation et le remplacer par un autre solvant mais il paraît bien préférable d'éliminer cette opération en préparant le dérivé Grignard dans le solvant même qui servira de milieu à la condensation ultérieure.

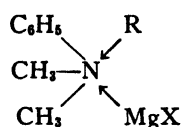
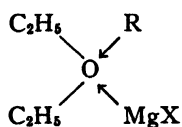
Brühl et Oordt (2) et Malmgren (7) furent les premiers à préparer un dérivé organomagnésien en l'absence d'éther mais ce fut surtout Tschelinzeff (15) qui montra d'une façon certaine la possibilité de préparer ces dérivés Grignard. Il montra que l'azote des amines tertiaires peut remplacer l'oxygène de l'éther dans la formule des RMgX . Il se servit pour cela de la diméthylaniline.

¹ *Manuscrit reçu le 21 février 1949.*

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² *Présentement à l'emploi de l'Institut de Microbiologie de l'Université de Montréal.*

Toutefois, dans certaines réactions, cet auteur peut diminuer la quantité de diméthylaniline à un point que ce composé ne peut plus jouer le rôle de support de la molécule mais sert plutôt de catalyseur de la réaction.



Spencer *et al.* (12, 13) et Oddo et Del Rosso (9) préparent les RMgX sans aucun solvant autre que l'halogénure. Stadnikov (14) emploie le xylène, Neogi (8) remplace la diméthylaniline par les iodures de trialkylsulfonium et le tétraphénylméthane; Hepworth (5) par les sulfures et les sulfinones organiques.

Gilman (3), Schlenk (10), Shorugin (11) et ses collaborateurs préparent les RMgX sans solvant; Andrianov (1) utilise le tétraéthoxysilicane. Enfin récemment Kuznetzov (6) revient à la diméthylaniline comme catalyseur de la réaction.

Dans notre travail nous avons repris surtout les travaux de Tschelinzeff (15) qui n'a préparé que l'iodure d'éthyle et de phénylmagnésium sans éther.

Dosages

Pour pouvoir traduire nos résultats en chiffres sûrs, nous avons dû nous assurer d'une bonne méthode de dosage des RMgX produits.

Gilman, Wilkinson, Fishel et Meyers (4), après une étude critique des cinq méthodes de titrage des organomagnésiens—titrage à l'iode, analyse gravimétrique, analyse indirecte, analyse volumétrique (Zerewitinoff), titrage par un acide—arrivent à la conclusion que les deux derniers procédés donnent des résultats satisfaisants.

Le titrage par un acide dans la méthode de Gilman consiste à titrer l'hydroxyde de magnésium formé par l'hydrolyse d'une quantité mesurée du dérivé RMgX par un excès connu d'acide sulfurique *N*/1 et à doser l'excès d'acide: c'est la méthode qui semble la plus pratique; dans le cas de dérivés RMgX peu solubles dans l'éther, qui comprennent une bonne partie des dérivés Grignard, Shorugin et ses collaborateurs (11) proposent une modification de la méthode qui consiste à solubiliser ces composés par un mélange à 50% en poids d'éther et de benzène (33 parties de ce mélange pour une partie de magnésium) et à procéder après un repos de 15 à 20 h. comme dans le dosage Gilman. Shorugin reconnaît cependant que souvent cette addition d'éther-benzène déclanche une nouvelle attaque du dérivé halogéné sur le magnésium et que le rendement ainsi peut être augmenté considérablement au cours du dosage lui-même. Nous avons constaté la même chose; comme dans notre cas, nous opérons précisément sans éther, l'addition de ce composé au cours du dosage déclanchait la réaction en faussant nos résultats; même l'addition et la conservation à 0° de la solution éther-benzène-RMgX, nous donnait des chiffres encore trop forts.

Nous avons essayé ensuite la méthode de dosage employée par Tschelinzeff. Celui-ci faisait réagir sur le magnésien obtenu, la benzaldéhyde, et établissait le rendement d'après la quantité de l'alcool secondaire formé. Cette nouvelle méthode de dosage donna des rendements un peu plus sûrs, mais incomplets; en effet l'obtention de l'alcool secondaire n'est pas une réaction quantitative.

Nous avons imaginé alors une technique particulière assez simple mais efficace pour obtenir le pourcentage réel du dérivé RMgX produit.

Après avoir procédé à l'hydrolyse du complexe obtenu dans la synthèse du RMgX, les copeaux de magnésium en excès sont séparés de l'hydroxyde de magnésium par lavage à l'eau dans un bécher; par décantations successives (six à sept), l'hydroxyde de magnésium, étant très fin, reste bien en suspension dans l'eau, alors que les copeaux de magnésium se déposent rapidement au fond du bécher. Cette opération se fait facilement avec un peu de pratique; un examen soigneux de l'hydroxyde décanté et laissé au repos n'a jamais montré des traces de copeaux de magnésium entraîné.

Le résidu de magnésium est recueilli sur un filtre, séché et pesé et un premier rendement est calculé d'après la quantité de magnésium consommé; l'hydroxyde de magnésium est solubilisé dans un excès d'acide sulfurique $N/1$, et titré en retour par l'hydroxyde de sodium $N/1$; nous obtenons ainsi un deuxième chiffre de rendement. On trouve toujours une différence plus ou moins grande entre les rendements calculés par les deux méthodes, premièrement par la quantité d'hydroxyde de magnésium formé après hydrolyse, deuxièmement par le magnésium disparu; elle s'explique par les réactions secondaires qui consomment plus de magnésium qu'indiqué par l'hydrolyse du complexe organomagnésien, produit principal de la réaction; les réactions secondaires donnent surtout du chlorure de magnésium et nous avons vérifié que ce composé n'affecte pas le dosage de l'hydroxyde de magnésium. Le rendement donné par le magnésium consommé est toujours plus élevé que celui donné par l'hydroxyde de magnésium de l'hydrolyse.

Notre méthode de dosage avec ces deux chiffres de rendements nous permet donc d'évaluer avec assez de précision le rendement final de la réaction et aussi chose précieuse, l'importance des réactions secondaires suivant les conditions de la préparation ou de la constitution du dérivé halogéné.

Partie expérimentale

Mode d'opération.—Les essais de synthèse ont été faits dans un appareil standard à joints normalisés, avec agitateur mécanique et dans une atmosphère d'azote séché par un passage dans des flacons laveurs à acide sulfurique; pendant nos expériences, nous avons remplacé les flacons d'acide sulfurique par des tours contenant du "Drierite", éliminant ainsi la possibilité d'entraînement de l'anhydride sulfureux. Nous opérons d'une façon constante avec 5 g. de magnésium (0.20 atome-gramme + 0.14 g. en excès), et une quantité calculée d'halogénure (0.20 mol. gramme). Dix molécules-grammes de solvant et 5 g. de l'halogénure sont mis en réaction dès le début et le reste est ajouté

d'une façon variable suivant les conditions de l'expérience; l'amorce est quelquefois difficile et varie suivant les solvants et le dérivé halogéné; la meilleure est l'iodure d'éthyle qu'on peut ajouter au début en proportion de 1% de l'halogénure employé.

Résultats

Nous avons fait 232 expériences avec divers solvants et dérivés halogénés avant d'arriver aux meilleures conditions de rendement maximum. Nous résumons les résultats dans le tableau suivant: le rendement est basé sur le chiffre donné par le titrage de l'hydroxyde de magnésium obtenu par l'hydrolyse du dérivé RMgX et est une moyenne des meilleurs rendements obtenus. Le chlorure de butyle tertiaire et le bromure d'allyle n'ont pas donné de rendements appréciables.

TABLEAU

RX	Solvant	$\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$, mol. g. (i)	Reflux, h.	T , °C.	Rendement, %
$\text{C}_2\text{H}_5\text{I}$	C_6H_6	0 05	5 - 7	80	82 (ii)
$\text{C}_2\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{CH}_3$	"	"	"	82
$\text{C}_2\text{H}_5\text{Br}$	C_6H_6	0 33	4 - 7	80	96 (ii)
$\text{C}_2\text{H}_5\text{Br}$	Éther de pétrole (80°-100°) (iii)	1	4 - 7	90 - 100	94
$n\text{-C}_4\text{H}_9\text{Cl}$ (iv)	C_6H_6	1 25	11 - 18 (v)	80	90 - 96
$n\text{-C}_4\text{H}_9\text{Cl}$	Éther de pétrole (80°-100°)	"	"	90 - 100	92
$sec\text{-C}_4\text{H}_9\text{Cl}$	C_6H_6	"	14	80	86
$iso\text{-C}_4\text{H}_9\text{Cl}$	"	"	"	"	80
$\text{C}_6\text{H}_5\text{Br}$	"	"	"	"	81
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	"	"	"	"	20-30 (vi)

NOTES

- (i) La diéthylaniline, la di-*n*-propylaniline et la di-*n*-butylaniline ont donné des résultats bien inférieurs à ceux fournis par la diméthylaniline.
- (ii) Avec l'iodure d'éthyle et le bromure d'éthyle la diméthylaniline joue le rôle de catalyseur de la réaction mais avec l'éther de pétrole, il faut ajouter assez de ce composé pour qu'il devienne le support de la réaction.
- (iii) L'éther de pétrole doit être très pur. Nous avons utilisé un éther de pétrole fourni par la British Drug House Ltd. L'éther de pétrole du commerce même purifié par distillation et traitement au permanganate de potassium nous a toujours donné des résultats inférieurs. Le magnésium en copeaux doit être aussi très pur sinon les rendements diminuent: le magnésium préparé pour les dérivés Grignard par la compagnie Dow nous a donné complète satisfaction.
- (iv) Le temps d'addition doit être uniforme pour éviter les réactions secondaires que nous constatons par la différence entre les deux rendements obtenus à l'analyse. Voici la meilleure méthode à suivre: ajouter 25% du composé au départ puis 35% après trois heures de reflux et les deux autres 20% après deux heures de reflux respectivement.
- (v) Les meilleurs résultats ont été donnés par 18 h. de reflux; de bons résultats ont été obtenus après 8 et 11 h., mais ils ne sont pas constants.
- (vi) La réaction est entravée par des réactions secondaires: les différences de dosage entre le chiffre donné par l'hydroxyde de magnésium et le magnésium résiduel différent de 35%. Le chlorure de benzyle réagit aussi sur l'amine pour donner un sel quaternaire solide qui nuit à la réaction. Le bromure d'allyle donne aussi avec l'amine un précipité solide qui arrête la réaction.

Condensations

Nous avons fait quelques condensations, afin d'étudier la réactivité des dérivés organomagnésiens préparés ainsi sans éther en présence de diméthylaniline.

Le propionate d'éthyle, en réagissant sur le $n\text{-C}_4\text{H}_9\text{MgCl}$ a donné un rendement de 75% en di- n -butyléthylcarbinol; l'acétone a donné 70% en diméthyl- n -butylcarbinol; la benzaldéhyde a donné un rendement de 66% en butyl- n -phénylcarbinol; et nous avons obtenu 64% en alcool amylique normal à partir du trioxyméthylène. Les deux derniers rendements sont un peu diminués à cause des difficultés rencontrées dans la distillation des produits finaux.

Ces expériences, tout en enlevant tout doute sur la réactivité des dérivés organomagnésiens préparés sans éther, prouvent que ces dérivés sont capables de réagir sur d'autres composés, et de donner des rendements comparables à ceux que l'on obtient dans l'éther.

Dans certaines condensations très vives, il y aurait avantage à utiliser des dérivés organomagnésiens solides, préparés dans un solvant dont le point d'ébullition est plus élevé que celui de l'éther; ces dérivés organomagnésiens étant peu solubles dans certains solvants, la réaction est plus modérée. L'utilisation des RMgX solides peut donc permettre un meilleur contrôle de la marche de certaines condensations trop vives.

Remerciements

Nous tenons à remercier l'Office scientifique de Recherches de la Province de Québec qui, par l'octroi d'une bourse de recherche à Jacques de Repentigny de 1944 à 1947, a permis la poursuite de ce travail, partie des conditions requises pour l'obtention du grade de Ph.D.

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THE REACTION OF NITROGEN ATOMS WITH ETHYLENE¹

J. H. GREENBLATT² AND C. A. WINKLER

Abstract

Reaction of nitrogen atoms with ethylene has been found to produce hydrogen cyanide, ethane, and a polymerizable material. The yield of hydrogen cyanide was approximately 70% of the ethylene consumed by nitrogen atoms, while the amount of polymerizable material averaged about 16% by weight of the hydrogen cyanide produced. The yield of ethane increased as the excess of ethylene over nitrogen atoms was increased. The reaction was found to proceed by "clean-up" of nitrogen atoms. An activation energy of 6.9 kcal. was calculated from collision yields, a steric factor of 0.1 being assumed. A mechanism for the reaction has been proposed, involving rupture of the ethylene double bond with formation of hydrogen cyanide and a methyl radical, the methyl radical then reacting further with nitrogen atoms.

Introduction

Although elementary reactions involving atoms and free radicals have been the subject of intensive investigation (18), few kinetic data for the reactions of nitrogen atoms are recorded in the literature. This is doubtless due to the fact that, for many years, it was uncertain whether atoms or metastable molecules were responsible for the enhanced chemical reactivity of nitrogen after it had been subjected to a condensed or electrodeless discharge.

The activity was assigned to metastable molecules when attempts were made to correlate the spectra of the afterglow in "active nitrogen" with its physical and chemical behavior. However, experimental evidence accumulated to indicate that the enhanced chemical activity was due to the presence of nitrogen atoms. The duration of afterglow for as much as six hours under suitable conditions (16), and the direct estimation of nitrogen atom concentrations up to 40% by pressure measurements (24) both favor the conclusion that "active nitrogen" contains atomic nitrogen. Moreover, a second discharge applied externally to the condensed discharge used to activate the nitrogen has been found to excite atomic nitrogen lines (3). The intensity of these lines was found to correlate with the intensity of the afterglow. No atomic nitrogen lines were found when a glowless discharge was used (3), and, in fact, such a discharge has been shown to produce no "active nitrogen" (15). A Stern-Gerlach experiment with active nitrogen, using a silver nitrate target, indicated the presence of nitrogen atoms (12, 13), while more recently (7) it has been shown by pressure measurements that practically complete dissociation of nitrogen into atoms can be obtained in an electrodeless discharge.

The only direct evidence in contradiction to the atomic hypothesis appears to be a failure to observe that decay of the afterglow depended upon triple

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collisions (4, 5). However, if the glowing gas is compressed, the intensity of the afterglow varies as $\frac{1}{(\text{volume})^2}$, and also metals such as copper and zinc quench the afterglow (8).

Plausible mechanisms to reconcile the atomic hypothesis with the afterglow excitation have been offered (7).

The reactions of nitrogen atoms with various hydrocarbons have been studied qualitatively by Strutt (20, 21, 22), who found hydrogen cyanide to be the main product, but made no kinetic studies of its formation. The present investigation represents the first of a series by which it is hoped to elucidate the mechanism of the degradation of hydrocarbons by nitrogen atoms.

Experimental

The reaction was studied by the Wood-Bonhoeffer method.

Commercial nitrogen was purified by passing it successively through alkaline sodium hydrosulphite, potassium hydroxide solution, and water. The gas then passed through a calibrated flowmeter and entered the discharge tube through a scratched stopcock.

Ethylene was obtained from the Ohio Chemical Company and from the Polymer Corporation, Sarnia. It was specified to be 99% pure and was used, after a single bulb to bulb fractionation. The rate at which ethylene was admitted from the storage bulb to the reaction vessel was controlled by a scratched stopcock, the amount used in given time being determined from measurements of the initial and final pressures of gas in the storage bulb.

Nitrogen atoms were produced by a high voltage condensed discharge. The electrical circuit consisted of a 4 μ f. condenser, which was charged by a 3500 v. half-wave rectifier through a 20,000 to 50,000 ohm resistance, and discharged through the discharge tube across a spark gap. The discharge occurred in pulses, the number of pulses per second depending on the value of the resistance in the circuit and the length of the spark gap. A pulse rate of four to five per second was found to be the most satisfactory.

The discharge tube was a Pyrex tube 70 mm. long and 20 mm. inside diameter, into the ends of which were sealed platinum wires carrying aluminum foil electrodes.

The reaction vessel was a 500 cc. bulb, connecting with the discharge tube through a tube 18 cm. long and 18 mm. diameter. This connecting tube was found necessary to prevent diffusion of ethylene back into the discharge tube. The reddish-violet color accompanying reaction of ethylene with nitrogen atoms was readily detected against the yellow background of the afterglow, and served to indicate the limit of back diffusion of the ethylene.

The products of reaction, together with unreacted ethylene, were withdrawn from the reaction vessel by a three stage mercury diffusion pump backed by an oil pump. The pump passed, on the average, 1.25 liters of gas (S.T.P.) per hour, at a pressure of about 0.5 mm. A liquid air cooled trap

between the reaction vessel and the diffusion pump removed part of the unchanged ethylene together with hydrogen cyanide and other products. The remainder of the gas stream passed through the diffusion pump into a trap containing silica gel and cooled with liquid air. The remainder of the ethylene and large amounts of nitrogen were removed in this trap.

The nitrogen atom concentration was measured with a Wrede gauge, a porous disk being used as a diffusion orifice (6) and the pressure differential across the orifice being measured with McLeod gauges. The atom concentrations were determined in the absence of ethylene, at a point about midway between the reaction vessel and the discharge tube. This position was chosen since at high ethylene concentrations it corresponded to a position almost immediately in front of the reaction zone indicated by the reddish-violet color; under such conditions the reaction vessel was colorless, the absence of nitrogen afterglow indicating the absence of nitrogen atoms beyond the reddish-violet reaction zone (3, 15). With low ethylene concentrations, hence less back diffusion, the atom concentration measured at the position chosen would be somewhat higher than the concentration immediately preceding the reaction zone, owing to some decrease in atom concentration between the point of measurement and the now more distant reaction zone. However, by analogy with the behavior of oxygen atoms (11), the extent of such decrease in atom concentration should be comparatively small.

After each experiment of one-half hour's duration, the total amount of gaseous products in the two traps was determined, followed by analysis of a sample in a Bone and Wheeler gas analysis apparatus. Ethylene was absorbed in mercuric nitrate-nitric acid solution. Combustion analysis of the gas mixture was also made.

Hydrogen cyanide collected in the first trap and was estimated gravimetrically by precipitation with silver nitrate added to the cold trap.

A white material also collected in the upper portion of the inlet tube of the trap, but this material liquefied and became yellow and viscous when attempts were made to distill it to the lower part of the trap. The amount of viscous (polymer) residue was determined by gathering it on to a weighed filter paper.

Results

The data presented in Table I show that, at given nitrogen atom concentration, the amount of hydrogen cyanide produced during a half-hour reaction period is essentially constant (within 10%) over a wide range of ethylene flow rates. The results in Table II show a similar approximate constancy for the amount of ethylene converted to hydrogen cyanide and other products, when the ethylene flow rate is varied as much as fivefold. A small increase in ethylene consumption does occur at higher ethylene flow rates, with corresponding increase in hydrogen cyanide production. This small increase at

TABLE I

PRODUCTION OF HYDROGEN CYANIDE AT VARIOUS NITROGEN ATOM
CONCENTRATIONS AND ETHYLENE FLOW RATES

Temperature: $22 \pm 2^\circ \text{C}$.

Total pressure, mm.	Nitrogen flow rate, moles $\times 10^{-2}$, per 30 min.	Nitrogen atom conc., %	Ethylene flow rate, moles $\times 10^{-2}$, per 30 min.	Hydrogen cyanide produced, moles $\times 10^{-2}$, per 30 min.
0.61	3.0	27	0.50	0.43
0.60	2.7	33	0.56	0.44
0.66	3.0	27	0.95	0.48
0.63	2.9	27	1.13	0.47
0.61	3.0	27	1.19	0.46
0.61	2.8	31	1.30	0.48
0.64	2.9	30	1.42	0.47
		(Av. = 29)		(Av. = 0.46)
0.54	2.8	23	0.75	0.40
0.54	2.8	21	0.76	0.37
0.55	2.8	18	0.92	0.35
0.66	3.0	22	0.95	0.35
0.53	2.9	22	1.05	0.39
0.57	2.9	23	1.18	0.41
		(Av. = 22)		(Av. = 0.38)
0.59	2.6	17	0.71	0.31
0.58	2.5	16	0.94	0.27
0.62	2.6	16	1.00	0.31
0.58	2.6	14	1.21	0.29
		(Av. = 16)		(Av. = 0.30)

TABLE II

CONSUMPTION OF ETHYLENE AND PRODUCTION OF HYDROGEN CYANIDE, SATURATED PRODUCTS,
AND POLYMERIZABLE MATERIAL AT VARIOUS ETHYLENE FLOW RATES
WITH GIVEN NITROGEN ATOM CONCENTRATION

Temperature = $22 \pm 2^\circ \text{C}$.

Total pressure, mm.	Nitrogen flow rate, moles $\times 10^{-2}$, per 30 min.	Nitrogen atom conc., %	Ethylene flow rate, moles $\times 10^{-2}$, per 30 min.	Ethylene recovered, moles $\times 10^{-2}$, per 30 min.	Ethylene reacted, moles $\times 10^{-2}$, per 30 min.	Ethylene converted to saturated products, moles $\times 10^{-2}$, per 30 min.	Ethylene converted to hydrogen cyanide, moles $\times 10^{-2}$, per 30 min.	Hydrogen cyanide produced, moles $\times 10^{-2}$, per 30 min.*	Hydrogen cyanide produced, gm. per 30 min.	Polymerizable material produced, gm. per 30 min.
0.64	3.0	29	0.29	0.00	0.29	0.00	0.29	0.43	0.116	0.012
0.60	2.8	31	0.30	0.00	0.30	0.00	0.30	0.43		
0.61	3.0	27	0.50	0.16	0.34	0.063	0.28	0.43		
0.60	2.7	33	0.56	0.23	0.33	0.049	0.28	0.44		
0.66	3.0	27	0.95	0.49	0.46	0.102	0.36	0.48	0.130	0.020
0.63	2.9	27	1.13	0.69	0.44	0.072	0.36	0.47	0.127	0.016
0.61	3.0	27	1.19	0.71	0.48	0.094	0.38	0.46	0.124	0.020
0.60	2.7	28	1.19	0.76	0.43	0.098	0.33			
0.61	2.8	31	1.30	0.74	0.56	0.120	0.35	0.48	0.130	0.026
0.63	2.9	30	1.42	0.89	0.53	0.165	0.37	0.47		

* The values in this column are not twice those in the preceding column, owing to the presence of polymerizable product.

higher flow rates is probably due to displacement of the reaction zone nearer to the discharge tube, where the atom concentration is slightly higher. Considered as a whole, the data indicate that reaction proceeds by a "clean-up" of nitrogen atoms.

A limiting value of the ethylene flow rate was found, below which the amount of hydrogen cyanide produced varied linearly with ethylene flow rate at given atom concentration. The data illustrating this behavior are plotted in Fig. 1. In the range represented, nitrogen atoms were in excess,

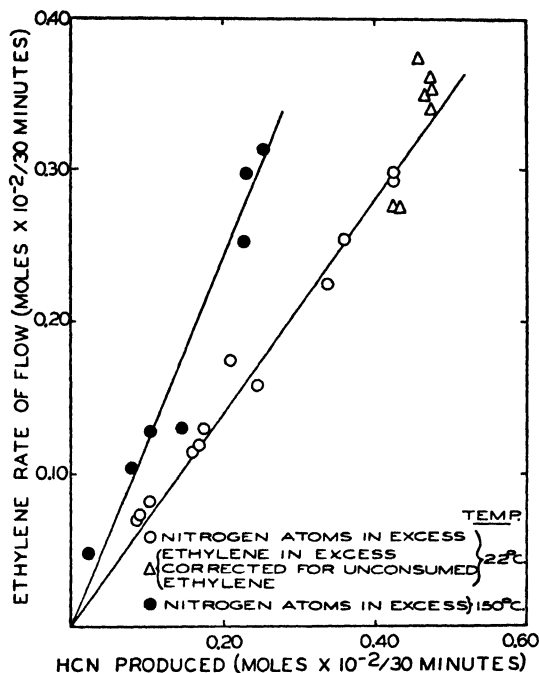


FIG. 1. Production of hydrogen cyanide at various ethylene flow rates at 22° C. and 150° C.

and all the ethylene was consumed. The plot therefore represents the maximum amount of hydrogen cyanide that can be obtained in the presence of excess nitrogen atoms. On the same figure are shown some values for the amount of ethylene converted to hydrogen cyanide and other products in experiments where ethylene was in excess (Table II). These points also lie satisfactorily close to the line, since in effect the values of ethylene flow rate have been corrected for unconsumed ethylene and ethylene converted to saturated products, i.e., corrected back to the critical limit of ethylene flow rate.

When the data of Fig. 1 are brought together with data from Tables I and II and from eight experiments for which details have not been given, the summary represented in Fig. 2 is obtained. In the additional eight experiments only ethylene input and hydrogen cyanide production were measured, but the

conditions under which the experiments were made were similar to those where the nitrogen atom concentrations averaged 22% and 16%, and the amounts of hydrogen cyanide produced per half-hour period agree with the values shown in Table I for these atom concentrations.

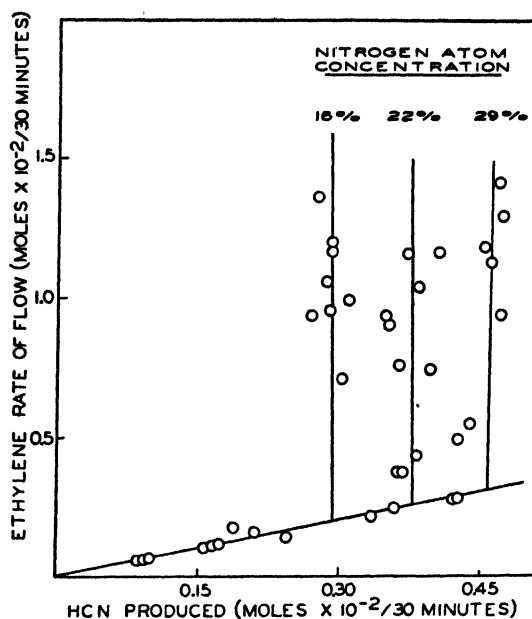


FIG. 2. Production of hydrogen cyanide at various ethylene flow rates and nitrogen atom concentrations.

In Fig. 2, the vertical lines show the constancy of hydrogen cyanide production, above a critical limit of ethylene flow rate, for three nitrogen atom concentrations. Such a vertical line could be realized experimentally at any atom concentration. A point on the sloping line, corresponding to any given atom concentration, defines the critical flow rate of ethylene below which consumption of ethylene is complete at that nitrogen atom concentration. The whole behavior reflected in Fig. 2 conforms to a "clean-up" reaction.

The saturated products were inferred from explosion analysis to consist almost entirely of ethane. If methane and hydrogen were products of the reaction they were either formed in amounts that were too small to be detected by this method of analysis, or they were not retained in the silica gel trap in the presence of large amounts of nitrogen. The amount of ethylene converted to saturated products increases from undetectable amounts at low ethylene flow rates to considerable amounts at high ethylene flow rates. However, the amount of ethylene converted to hydrogen cyanide and products other than saturated hydrocarbons remains relatively constant, as does also the amount of hydrogen cyanide obtained. It would seem, therefore, that the production of saturated products does not occur in the same reaction as that in which hydrogen cyanide is produced.

Estimation of the polymerizable material, although only approximate, leaves little doubt that it is produced in comparatively small amount, and that hydrogen cyanide is to be considered as the main product of the reaction.

The reaction was also studied at 150° C. The results are shown in Fig. 1 together with those obtained at the lower temperature. It will be noted that, at the higher temperature, a smaller amount of hydrogen cyanide was obtained from a given amount of ethylene in the presence of excess nitrogen atoms.

Calculations of collision yields were made for only a few of the experiments. With "clean-up" occurring, the amount of ethylene consumed by reaction with nitrogen atoms is constant above the critical value of ethylene flow rate. Thus, while percentage conversions of ethylene based on total ethylene flow are variable, the percentage conversions based on ethylene consumed by nitrogen atoms remain constant. Since, at high ethylene concentrations, only a portion of the reaction vessel is occupied by the reacting gases, the calculations were made for experiments at the critical ethylene flow rate, when the reacting gases filled the reaction vessel and a more accurate estimate of reaction time was possible. Under these conditions, all the ethylene reacts, but only about 75% of it is converted to hydrogen cyanide. It is, then, a question whether formation of the remaining products depends upon the same rate controlling step as formation of hydrogen cyanide, i.e., a step involving reaction with a nitrogen atom. If it does, then the conversion could be taken as 100%, only 75% of the products emerging as hydrogen cyanide. If, however, hydrogen cyanide is formed by a different initiating reaction, the percentage conversion for the main reaction would be 75%. Calculations were made using both 75% and 100% conversion values. These calculations should give an upper and lower limit respectively for the activation energy.

The number of collisions per second of one ethylene molecule with nitrogen atoms is given by

$$Z_{C_2H_4-N} = 2\sqrt{2\pi} \cdot N_N \left(\frac{d_N + d_{C_2H_4}}{2} \right)^2 \left(\frac{M_N + M_{C_2H_4}}{M_N \cdot M_{C_2H_4}} \cdot RT \right)^{1/2}$$

where M_N and $M_{C_2H_4}$ are the respective molecular weights of the nitrogen atom and ethylene molecule, d_N and $d_{C_2H_4}$ their molecular diameters, and N_N is the number of nitrogen atoms per cubic centimeter. The value of d_N was taken as 2.98×10^{-8} cm.; from Rayleigh's assumed value for the coefficient of self-diffusion of nitrogen atoms (17). A value of 3.5×10^{-8} was used for $d_{C_2H_4}$ (14). The activation energies were calculated from the relation

$$\text{Collision yield} = A e^{-E/RT}$$

a value of 0.1 being assumed for the steric factor, A .

The data used for the calculations and the results obtained are given in Table III.

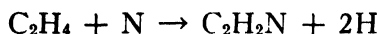
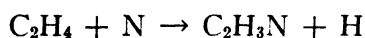
Discussion

Both the upper limit of 7.0 kcal. and lower limit of 6.8 kcal. calculated for the activation energy may be regarded as too high, since the atom concentration used in the calculations is that measured near the entrance to the reaction vessel during experiments in which no ethylene was flowing, and is not the average concentration during reaction. In the experiments for which the calculations were made the ethylene flow rate was just at the critical limit. Hence consumption of nitrogen atoms was practically complete, and the steady state concentration of nitrogen atoms probably much lower than the value used in the calculations.

The value of 0.1 taken for the steric factor is also suspect. While this is the value that it has been customary to assume for calculating activation energies from collision yields in analogous hydrogen atom reactions, there are reasons to believe that a smaller steric factor should be used (18, 20, 21, 22). The adoption of a smaller steric factor would result in a lower value of the calculated activation energy.

An attempt to formulate a mechanism for the reaction between nitrogen atoms and ethylene is handicapped by lack of experimental data on the strength of carbon-nitrogen bonds, and by lack of kinetic data on nitrogen atom reactions generally. It is possible, however, to suggest a mechanism that can account reasonably well for the experimentally observed results.

The most recent estimates (18) for bond strengths give values ranging from 90 to 100 kcal. for the C-H bond, about 80 kcal. for the C-C bond and about 60 kcal. (9) for the C-N bond. Hence, all reactions involving replacement of one or more hydrogen atoms by nitrogen would be endothermic. Examples of such possible reactions are:



Such reactions are endothermic by as much as 30 kcal. or more, hence do not appear probable as the initial step in a "clean-up" reaction.

A second possibility is the addition of a nitrogen atom to form an activated complex, perhaps of free radical type:

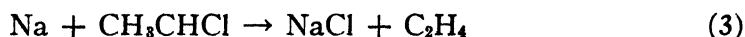


This reaction would be exothermic. It could be followed by a rearrangement to split off hydrogen cyanide, or by a second collision with a nitrogen atom to form two molecules of hydrogen cyanide and two hydrogen atoms. The probability of this second collision is smaller than the probability of (1), owing to depletion of nitrogen atoms by (1). Moreover, if the necessary collision did occur the reaction would be about 40 kcal. endothermic, with a

correspondingly small probability of occurrence. Thus, rearrangement of the activated complex in (1) with formation of hydrogen cyanide appears more probable. The initial step might therefore be represented:

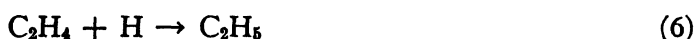
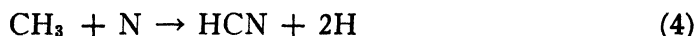


This reaction actually involves the simultaneous rupture of a double bond and migration of a hydrogen atom, and is about 25 kcal. exothermic. One-step mechanisms of this type, in which scission and re-formation of bonds occur with simultaneous migration of hydrogen atoms, have been proposed by Bawn and Milsted (2) and by Bawn and Dunning (1) to account for ethylene formation in reactions of the type

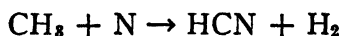


Ethylene is obtained even when hydrogen is used as the carrier gas. These authors take this as evidence for the absence of a CH_3CH radical, on the grounds that if it were present ethane should be formed.

Following upon (2), the following reactions might be assumed to occur:



Reaction (4) is suggested in preference to the reaction



since assumption of the latter makes it difficult to account for the observed increase in amount of saturated products with increased excess ethylene. Reaction (4) should have a high probability since consumption of ethylene is complete when nitrogen atoms are in excess. If (5) occurred, under these conditions of excess nitrogen atoms, the higher hydrocarbons formed would also be broken down to hydrogen cyanide by reaction with nitrogen atoms. With excess ethylene present Reaction (5) might be expected, leading to the formation of higher hydrocarbons, which were not found however, among the products. The nonoccurrence of (5) can be explained by the observation that under these conditions the reaction zone occupied only a small portion of the reaction vessel and a portion of the connecting tube. This means that at high ethylene concentrations the ethylene diffused out of the reaction vessel against the gas stream, towards the discharge tube, the reddish violet reaction zone marking the extent of mutual penetration before complete consumption of one or other component. Thus, in this zone there exists no large excess of ethylene, and Reaction (5) would have small probability.

The ethane formed when ethylene was in excess was presumably formed by hydrogenation of ethylene, as in Reactions (6) and (7). The hydrogenation of ethylene has recently been reviewed by Steacie (18), the general conclusion being that the nature of the products obtained depends upon the hydrogen-ethylene ratio. At moderate hydrogen concentrations, ethane is formed exclusively. Reaction (6) occurs readily, and has been assigned an activation energy of about 5 kcal. (18).

The amount of polymerizable material formed in a given time by the reaction of nitrogen atoms with ethylene was probably constant, since the yield of hydrogen cyanide (about 70% of the ethylene consumed by nitrogen atoms) was reasonably constant. Difficulty in handling the small amount of material obtained during an experiment made it impossible to obtain a sample that could be considered sufficiently pure to justify an analysis of it. Consequently, nothing is known about the composition or probable mechanism of formation of the polymerizable material.

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APPLICATION OF DIFFUSION FLAME TECHNIQUE TO THE REACTION BETWEEN NITROGEN ATOMS AND ETHYLENE¹

J. H. GREENBLATT² AND C. A. WINKLER

Abstract

Rate constants for the reaction between nitrogen atoms and ethylene have been obtained by diffusion flame technique over the temperature range 273° to 373° C. An activation energy of about 3 kcal. has been obtained from the temperature coefficient of these rate constants, and using this value a steric factor of 10^{-2} has been calculated.

Introduction

The diffusion flame method of measuring reaction rates was developed originally by Polanyi and coworkers for studying the reactions between sodium atoms and various organic halides (2, 3, 4, 5). The rate constant was inferred from measurements of the distance one component diffused into another before being consumed by reaction. Obviously, successful application of the method requires demarcation of the reaction zone from the surrounding gas. In the method as originally developed, a carrier gas was passed through liquid sodium at 250° C. and then through a jet coaxially mounted in a larger tube, where the sodium vapor diffused into, and reacted with, the organic halide. The extent of diffusion was determined by exciting fluorescence in the sodium vapor with a resonance lamp.

It is evident that the extent of mutual penetration of the vapors should be greater, the slower the reaction rate. In formulating this relation, three assumptions must be made:

(i) The flow of inert gas should be fast enough to prevent diffusion of the organic halide back into the jet. The concentration of the emergent sodium vapor is then not decreased by reaction within the jet.

(ii) The rate of flow of carrier gas in the tube surrounding the jet should be slow enough that distribution of the reactants occurs by diffusion only, the influence of mass flow being negligible. If the distribution of the halogen compound is not influenced by the flow then, if its consumption by sodium vapor is ignored, it should have the same partial pressure, p_{Hal} , throughout the reaction space.

(iii) The flame diameter should be smaller than that of the reaction vessel, to eliminate influence of the wall.

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By applying steady state calculations for the condition that the partial pressure of the halogen compound is constant at p_{Hal} throughout the reaction space and drops to zero at the jet, Hartel and Polanyi (3) obtained

$$k = \frac{\left(\ln \frac{p_{\text{jet}}}{p_0}\right)^2}{\frac{d^2}{4}} \cdot \frac{D}{p_{\text{Hal}}},$$

where p_{jet} = partial pressure of sodium vapor at the jet,

p_0 = partial pressure of sodium vapor at the edge of the flame,

p_{Hal} = partial pressure of the halide,

d = diameter of the flame,

D = diffusion coefficient of the sodium vapor under the conditions of the experiment.

As reported previously (1), the reaction between nitrogen atoms and ethylene is accompanied by a reddish violet color that may be differentiated reasonably well from the yellow afterglow associated with the presence of nitrogen atoms. This suggested that diffusion flame technique might be applied to the reaction between nitrogen atoms and ethylene. In this way, by evaluating the activation energy, it was hoped to obtain a direct estimate of the steric factor for the reaction.

Experimental

Nitrogen atoms were produced by the Wood-Bonhoeffer method, as described previously (1). The pumping system and methods of gas purification, flow control, and measurement of atom concentration are all outlined in the previous paper.

It was necessary to make one modification to the apparatus used for the earlier study. The reaction vessel for the present study consisted of a tube 55 mm. in diameter and about 30 cm. long. Into one end was sealed coaxially a jet of 2.5 mm. diameter through which the ethylene was introduced into the reaction vessel. The yellow mixture of nitrogen atoms and nitrogen molecules was pumped from the discharge tube, through a wide connecting tube, to the reaction vessel, which was connected directly to the pumping system by large diameter tubing, without any trapping system in the line. It was surrounded with a jacket fitted with a heating coil and a large window through which observations of the flame size could be made.

By proper regulation of the rates of flow of both gases, reasonably spherical flames were produced. The diameters of the flames were measured directly with a centimeter scale. Although it is hoped to improve upon this method in future studies of similar systems, it was found that, with some practice and in a darkened room, the dimensions of the reaction zone could be approximately determined by this simple procedure. The reddish-violet color of the reaction zone has been identified with the cyanogen spectrum (6, 7, 8) and appears to

be observed generally in the attack of hydrocarbons by nitrogen atoms, the end product being hydrogen cyanide. The cyanogen spectrum was also observed when cyanogen was introduced into a vessel containing nitrogen atoms, but was not obtained when hydrogen cyanide was used in place of cyanogen. Hence, the reddish violet color can be associated with reactions involving the formation of a carbon-nitrogen bond. The flame boundary may then be taken to represent the limit of diffusion of a hydrocarbon or a free radical derived from the hydrocarbon into the nitrogen atom mixture. A rate constant calculated from the flame diameter should therefore give the rate of the over-all reaction.

The various partial pressures required for calculating a rate constant were obtained from the experimentally evaluated total pressures and mole fractions. For ethylene, the pressure so obtained would be the pressure of ethylene in the system with no reaction occurring, and it was assumed that this was the emergent pressure at the jet. The limiting pressure of ethylene was obtained by decreasing the rate of ethylene flow until the small reaction zone was practically indistinguishable from the yellow background of the afterglow. The partial pressure of ethylene (9×10^{-4} mm.) at this very low flow rate was taken as that at the edge of the reaction zone where the reddish-violet and yellow colors merged.

The diffusion coefficient used in the calculations was that for self-diffusion of ethylene. This seems reasonable, since nitrogen and ethylene have the same molecular weight and almost identical collision diameters, and the concentration of nitrogen atoms is small compared with that of nitrogen molecules. Collision diameters for ethylene, taken from Landolt-Börnstein (Roth-Scheel) Tabellen, average 3.5×10^{-8} cm. while values for nitrogen range from 3.1 to 3.8×10^{-8} cm.

Results and Discussion

The experimental conditions and results are given in Table I. There is little doubt that the absolute values of the rate constants are considerably in error, but they are almost certainly not in error by a factor exceeding three or four. The relative values at different temperatures are of greater interest, since they indicate that the increase in rate constant over the temperature range studied is of the same order of magnitude as variations in the value of the rate constant at a given temperature. It can safely be stated that the rate constant does not increase by more than a factor of two or three over the range studied. This fact indicates an activation energy lower than the value of 6.9 kcal. calculated from collision yields for the reaction (1).

The values for the rate constants at the higher temperatures are more likely to be in error than those at lower temperatures, owing to the difficulty of obtaining a reasonably large spherical reaction zone with the smaller atom concentrations at the higher temperatures. Hence, only the range from 273° to 325° K. will be considered for obtaining a value of the activation energy.

TABLE I
EXPERIMENTAL CONDITIONS AND RATE CONSTANTS FOR REACTION OF NITROGEN ATOMS WITH ETHYLENE IN DIFFUSION FLAME

Nitrogen flow rate, moles/sec. $\times 10^4$	Nitrogen atom conc., %	Nitrogen atom flow rate, moles/sec. $\times 10^4$	Ethylene flow rate, moles/sec. $\times 10^4$	Total flow rate— corrected for nitrogen atoms, moles/sec. $\times 10^4$	Total pressure, mm.	p_N , mm.	$p_{C_2H_4}$, mm.	d , cm.	D_i , (calc.)	k , sec. ⁻¹ mm. ⁻¹	Average k , sec. ⁻¹ mm. ⁻¹
Temperature = 273° K.											
4.04	21	0.94	0.088	4.60	0.74	0.152	0.0142	4.3	88	0.95×10^3	1.4×10^3
4.04	21	0.94	0.129	4.64	0.75	0.153	0.0208	3.6	87	1.7×10^3	
4.04	21	0.94	0.096	4.61	0.74	0.151	0.0155	3.7	88	1.4×10^3	
Temperature = 295° K.											
4.14	20	0.92	0.111	4.61	0.76	0.151	0.0183	3.5	96	1.9×10^3	1.3×10^3
4.16	20	0.92	0.118	4.74	0.71	0.139	0.0178	5.0	103	1.1×10^3	
4.16	20	0.92	0.113	4.74	0.78	0.151	0.0185	4.5	94	1.1×10^3	
4.15	20	0.92	0.137	4.75	0.71	0.137	0.0206	5.1	104	1.2×10^3	
Temperature = 298° K.											
4.04	21	0.94	0.098	4.61	0.85	0.173	0.0180	4.8	87	0.8×10^3	1.1×10^3
3.99	21	0.93	0.067	4.52	0.81	0.167	0.0120	3.4	90	1.3×10^3	
Temperature = 325° K.											
4.10	14.5	0.65	0.064	4.45	0.74	0.107	0.0106	5.0	117	1.1×10^3	1.3×10^3
4.05	14.5	0.64	0.072	4.44	0.74	0.107	0.0121	5.7	116	0.9×10^3	
4.05	14.5	0.64	0.054	4.42	0.74	0.106	0.0090	3.5	117	1.9×10^3	
Temperature = 328° K.											
4.31	14	0.65	0.080	4.71	0.76	0.105	0.0128	3.4	112	2.6×10^3	3.1×10^3
4.36	14	0.65	0.064	4.75	0.80	0.110	0.0109	2.6	107	3.6×10^3	
Temperature = 348° K.											
3.89	10	0.41	0.044	4.04	0.90	0.091	0.0096	5.2	105	1.0×10^3	1.0×10^3
Temperature = 377° K.											
3.88	7	0.28	0.029	3.95	0.90	0.064	0.0065	4.2	117	1.6×10^3	1.6×10^3

For the rate constant to double over this range of temperature, the activation energy must be about 3 kcal. An activation energy of 3 kcal. would give a ratio of $\frac{k_{328}}{k_{273}} = 2.5$, while an activation energy of 2.5 kcal. would give $\frac{k_{328}}{k_{273}} = 2.1$. Thus, an activation energy of not more than 3 kcal. is indicated.

Values of the steric factor were calculated from the rate constants in Table I, a value of 3 kcal. being assumed for the activation energy. The steric factors were calculated by expressing the rate constant as

$$k = pZ \cdot e^{-E/RT},$$

where p is the steric factor and Z the collision number per second, given by

$$Z = d_{av}^2 \left(8\pi RT \frac{M_N + M_{C_2H_4}}{M_N \cdot M_{C_2H_4}} \right)^{1/2}$$

for one molecule of each reactant per cubic centimeter. The mean collision diameter, d , was obtained from the values 2.98×10^{-8} cm. and 3.5×10^{-8} cm. for nitrogen atoms and ethylene respectively. The calculated steric factors are given in Table II. The tabulated values indicate that a steric factor slightly higher than 10^{-2} is associated with the reaction followed by the dilute flame technique.

TABLE II

VALUES OF k IN SEC.^{-1} ($\text{MOLECULES/CC.})^{-1}$ AND CORRESPONDING STERIC FACTORS AT VARIOUS TEMPERATURES

$T, ^\circ\text{K.}$	$p, \times 10^{-2}$	$k, \text{sec.}^{-1}(\text{molecules/cc.})^{-1}$
273	2.7	2.68×10^{-14}
273	3.0	4.96×10^{-14}
273	3.9	3.86×10^{-14}
295	3.4	5.72×10^{-14}
295	1.9	3.22×10^{-14}
295	2.1	3.47×10^{-14}
295	2.1	3.50×10^{-14}
298	1.4	2.41×10^{-14}
298	2.1	3.81×10^{-14}
325	1.3	3.55×10^{-14}
325	2.3	6.36×10^{-14}
325	1.1	2.98×10^{-14}
328	3.0	8.80×10^{-14}
328	4.0	1.17×10^{-13}

If, in the previous study (1), a steric factor of 10^{-2} , instead of 10^{-1} , had been used, to calculate the activation energy from collision yield data, a value of 5.5 kcal. would have been obtained. There remains, therefore, a discrepancy of 2.5 kcal. between the value of 3 kcal. indicated by the present study and the recalculated value for the previous investigation. This corresponds to a difference in collision yields of approximately 10^2 for the two investigations.

There is no reason to suppose that this discrepancy has any significance other than to indicate the limitations of the data obtained by the two methods of studying the reaction. The rather drastic assumptions made in calculating the rate constants from the diffusion flame data should affect the absolute values of the rate constants much more than the relative values for different temperatures. Since the absolute values were used to calculate the steric factor of approximately 10^{-2} , it is possible that this value is considerably in error. Also, the activation energies obtained from collision yield data are doubtless too high, since the values for nitrogen atom concentrations used in the calculations were those measured in the absence of reaction. It might be argued that a similar consideration should apply to the diffusion flame method, even though, in this case, the reaction zone is surrounded by an excess of nitrogen atoms at essentially constant partial pressure. However, in the diffusion flame system, nitrogen atoms can be at least partially replenished in the flame by diffusion all around the periphery of the reaction zone, a condition that does not obtain in the first type of system used. The diffusion flame method should therefore be less subject to error from discrepancies between the measured atom concentrations and those actually present during reaction.

Everything considered, it seems reasonable to assign an activation energy of 3 to 5 kcal., with a steric factor not exceeding 10^{-2} , to the reaction of nitrogen atoms with ethylene.

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SOME AROMATICALLY SUBSTITUTED β -CHLOROPHENETOLES¹

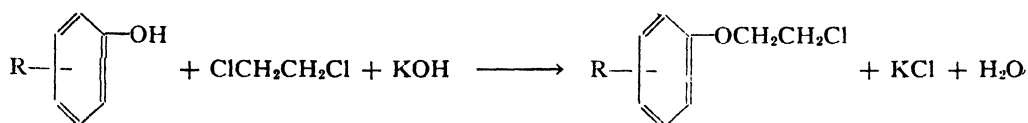
BY G. R. HARRIS AND ROSS STEWART²

Abstract

Six compounds derived from β -chlorophenetole have been synthesized from ethylene dichloride and the appropriate phenol. These are the *o*-methyl, *m*-methyl, *p*-methyl, *o*-methoxy, *p*-methoxy, and *o*-chloro derivatives of β -chlorophenetole.

In connection with polymerization studies on vinyl ethers it became necessary to prepare appreciable quantities of aromatically substituted β -chlorophenetoles as intermediates.

The method of synthesis adopted in this work is a modification of that of Wohl and Berthold (5). These workers prepared the parent compound, β -chlorophenetole (I), by heating equimolar quantities of phenol and ethylene dichloride to 110° C. with sodium hydroxide solution. It was found by the present authors, in agreement with a previous report on similar compounds (1), that under these conditions considerable amounts of ethylene glycol diphenyl ether were formed. The modified procedure entails the use of two moles of phenol and four moles of ethylene dichloride and was extended to six aromatically substituted phenols.



I R = H

II R = *o*-CH₃

III R = *m*-CH₃

IV R = *p*-CH₃

V R = *o*-CH₃O

VI R = *p*-CH₃O

VII R = *o*-Cl

The excess of ethylene dichloride serves a dual role: it reduces the formation of the corresponding ethylene glycol diphenyl ether to a negligible amount and it acts in the role of a solvent, allowing the product to be washed free of unreacted phenol with sodium hydroxide solution. This method is useful for preparing large quantities of these ethers in that it enables more moderate reaction temperatures to be employed than were required in the unmodified

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procedure (5). Although the yields are not high an exceedingly pure product is readily obtained. An increased ratio of the dichloride to the phenol (4 : 1) and longer refluxing periods had no effect on yields.

Experimental

The phenol (2 moles), ethylene dichloride (396 gm., 4 moles), potassium hydroxide (123 gm., 2.2 moles), and 300 ml. of water were heated under reflux for 26 hr. on the hot plate. The mixture was cooled, the layers separated (addition of water was sometimes required to effect a separation), and the oil layer was washed free of any unreacted phenol with hot 10% sodium hydroxide solution. The excess ethylene dichloride was removed by distillation and the residue was twice distilled, the second colorless distillate being collected over a one degree range. Those products that were solids were then crystallized from an ethanol-water mixture.

Results

The boiling points, yields, and analytical results for all of the products are listed in Table I.

TABLE I

No.	Name	B.p., °C.	Yield,* %	Formula	Analysis, % Cl†	
					Calc.	Found
II	<i>o</i> -Methyl- β -chlorophenetole‡	230–231	50	$C_9H_{11}OCl$	—	—
III	<i>m</i> -Methyl- β -chlorophenetole	235–236	50	$C_9H_{11}OCl$	20.79	20.69
IV	<i>p</i> -Methyl- β -chlorophenetole	236–237	46	$C_9H_{11}OCl$	20.79	20.73
V	<i>o</i> -Methoxy- β -chlorophenetole	254–255	55	$C_9H_{11}O_2Cl$	19.04	18.90
VI	<i>p</i> -Methoxy- β -chlorophenetole	286–287	55	$C_9H_{11}O_2Cl$	19.04	18.90
VII	<i>o</i> -Chloro- β -chlorophenetole§	251–252	55	$C_8H_8OCl_2$	37.10	37.06

* All yields calculated on quantity of product obtained after second distillation over a one degree range.

† Method of Drogin and Rosanoff (4).

‡ Previously prepared by Clemo and Perkin (2), b.p. 227° to 229° C. (762 mm.).

§ Reported by Coleman and Stratton (3), b.p. 142° to 144° C. (21.5 mm.), no analysis given.

The melting points and crystalline form of those products that were solids at room temperature are listed in Table II.

TABLE II

No.	M.p., °C.*	Crystalline form
IV	44 – 45	Colorless platelets
V	40 – 41	Colorless needles
VI	49 – 50	Colorless platelets

* All melting points are corrected.

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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS¹

BY PAUL E. GAGNON AND BENOIT NOLIN²

Abstract

α -Substituted cyanoacetic esters have been used to prepare hydrazides, azides, urethanes, and the 10 following α -amino acids: *dl*- α -aminocaprylic acid, *dl*- α -aminopelargonic acid, *dl*- α -aminocapric acid, *dl*- α -aminolauric acid, *dl*- α -(2-ethyl-*n*-butyl)- α -aminoacetic acid, *dl*- α -(2-ethyl-*n*-hexyl)- α -aminoacetic acid, *dl*- α -amino- γ -phenylbutyric acid, *dl*- α -amino- γ -benzylbutyric acid, *dl*-C-cyclohexylglycine, and *dl*- α -amino- β -1-naphthylpropionic acid. When a mixture of formic and hydrochloric acids and water was used, instead of hydrochloric acid, as hydrolyzing agent to transform the urethanes into amino acids, the period of heating was relatively short. The following compounds, as far as the authors are aware, have been prepared for the first time: ethyl α -cyanocaprylate, α -cyanocaprylamide, α -cyanocaprylic hydrazide, anisal α -cyanocaprylic hydrazide, benzal α -cyanocaprylic hydrazide, α -cyanocaprylic azide, α -carbethoxyaminocaprylonitrile, 5-(*n*-hexyl)-hydantoin, ethyl α -cyanopelargonate, α -cyanopelargonic hydrazide, anisal α -cyanopelargonic hydrazide, benzal α -cyanopelargonic hydrazide, isopropylidene α -cyanopelargonic hydrazide, α -cyanopelargonic azide, α -carbethoxyaminopelargonitrile, 5-(*n*-heptyl)-hydantoin, α -cyanocapric hydrazide, anisal α -cyanocapric hydrazide, benzal α -cyanocapric hydrazide, α -cyanocapric azide, α -carbethoxyaminocapronitrile, *dl*- α -phenylureidocapric acid, ethyl α -cyanolaurate, α -cyanolauric hydrazide, anisal α -cyanolauric hydrazide, α -cyanolauric azide, α -carbethoxyaminolauronitrile, *dl*- α -phenylureidolauric acid, ethyl α -(2-ethyl-*n*-butyl)- α -cyanoacetate, α -(2-ethyl-*n*-butyl)- α -cyanoacetic hydrazide, anisal α -(2-ethyl-*n*-butyl)- α -cyanoacetic hydrazide, benzal α -(2-ethyl-*n*-butyl)- α -cyanoacetic hydrazide, α -(2-ethyl-*n*-butyl)- α -cyanoacetic azide, α -(2-ethyl-*n*-butyl)- α -carbethoxyaminoacetoneitrile, *dl*- α -(2-ethyl-*n*-butyl)- α -aminoacetic acid, *dl*- α -(2-ethyl-*n*-butyl)- α -phenylureidoacetic acid, 5-(2-ethyl-*n*-butyl)-hydantoin, ethyl α -(2-ethyl-*n*-hexyl)- α -cyanoacetate, α -(2-ethyl-*n*-hexyl)- α -cyanoacetic hydrazide, anisal α -(2-ethyl-*n*-hexyl)- α -cyanoacetic hydrazide, α -(2-ethyl-*n*-hexyl)- α -cyanoacetic azide, α -(2-ethyl-*n*-hexyl)- α -carbethoxyaminoacetoneitrile, *dl*- α -(2-ethyl-*n*-hexyl)- α -aminoacetic acid, 5-(2-ethyl-*n*-hexyl)-hydantoin, *dl*- α -(2-ethyl-*n*-hexyl)- α -phenylureidoacetic acid, ethyl α -cyano- γ -phenylbutyrate, α -cyano- γ -phenylbutyrylhydrazide, anisal α -cyano- γ -phenylbutyrylhydrazide, benzal α -cyano- γ -phenylbutyrylhydrazide, α -cyano- γ -phenylbutyric azide, α -carbethoxyamino- γ -phenylbutyronitrile, 5-(β -phenylethyl)-hydantoin, *dl*- α -phenylureido- γ -phenylbutyric acid, ethyl α -cyano- γ -benzylbutyrate, α -cyano- γ -benzylbutyrylhydrazide, anisal α -cyano- γ -benzylbutyrylhydrazide, α -cyano- γ -benzylbutyric azide, α -carbethoxyamino- γ -benzylbutyronitrile, 5-(γ -phenylpropyl)-hydantoin, α -cyclohexyl- α -cyanoacetamide, α -cyclohexyl- α -cyanoacetic hydrazide, anisal α -cyclohexyl- α -cyanoacetic hydrazide, α -cyclohexyl- α -cyanoacetic azide, α -cyclohexyl- α -carbethoxyaminoacetoneitrile, *dl*- α -cyclohexyl- α -phenylureidoacetic acid, ethyl α -cyano- β -1-naphthylpropionate, α -cyano- β -1-naphthylpropionhydrazide, anisal α -cyano- β -1-naphthylpropionhydrazide, α -cyano- β -1-naphthylpropionic azide, α -carbethoxyamino- β -1-naphthylpropionitrile, and *dl*- α -phenylureido- β -1-naphthylpropionic acid.

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Introduction

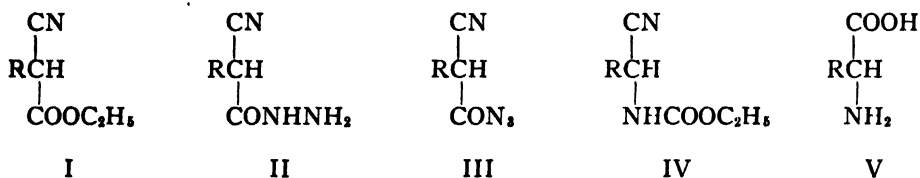
The decomposition of acid azides into isocyanates and nitrogen is known as the Curtius rearrangement. The reaction is a preparative method for isocyanates and compounds derived from them, such as urethanes, ureas, amides, and amines. When followed by hydrolysis, the Curtius rearrangement becomes a practical procedure for replacing a carboxyl group by an amino group. The whole process of converting an acid into its azide and an amine is commonly referred to as the Curtius reaction.



The synthesis of amino acids from substituted cyanoacetic esters by the Curtius reaction was first suggested by Darapsky and Hillers who synthesized glycine from cyanoacetic ester (2).

So far, 21 α -amino acids have been prepared by the Darapsky method (1, 4, 5, 6). The present paper deals with the synthesis of 10 other α -amino acids by the same method and is a contribution to the study of its general character.

The starting materials, the substituted cyanoacetic esters (I), were prepared by the condensation of organic halides with ethyl cyanoacetate in the presence of sodium ethylate. The yields varied from 45 to 78%.



R = *n*-hexyl, $\text{CH}_3(\text{CH}_2)_5-$; *n*-heptyl, $\text{CH}_3(\text{CH}_2)_6-$; *n*-octyl, $\text{CH}_3(\text{CH}_2)_7-$; *n*-decyl, $\text{CH}_3(\text{CH}_2)_9-$; 2-ethyl-*n*-butyl, $\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2-$; 2-ethyl-*n*-hexyl, $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2-$; β -phenylethyl, $\text{C}_6\text{H}_5(\text{CH}_2)_2-$; γ -phenylpropyl, $\text{C}_6\text{H}_5(\text{CH}_2)_3-$; cyclohexyl, $\text{C}_6\text{H}_{11}-$; 1-methylnaphthyl, $\text{C}_{10}\text{H}_7\text{CH}_2-$.

The formation of hydrazides (II) from the starting materials took place at room temperature merely by mixing the esters (I) with hydrazine hydrate. All the hydrazides were identified by condensing them with suitable reagents.

The conversion of the hydrazides into the corresponding azides (III) took place smoothly by treatment with nitrous acid, the azides being extracted with ether. On boiling the alcoholic solutions of the azides under reflux, the ethyl urethanes were formed.

The hydrolysis of the urethanes with hydrochloric acid required long periods of heating to get the highest possible yields in amino acids (V). In two cases, a mixture of equal volumes of concentrated hydrochloric acid, formic acid (85%), and water was used to obtain better yields.

TABLE I
ETHYL α -SUBSTITUTED CYANOACETATES, $\text{RCH}(\text{CN})\text{COOC}_2\text{H}_5$

R	Starting material	Yield, %	B.p., ° C.	Formula	Nitrogen, %		n_D^{20}
					Calc.	Found	
<i>n</i> -Hexyl	$\text{CH}_3(\text{CH}_2)_5\text{Br}$	70	149–150 (19 mm.)	$\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}$	7.10	7.17	1.4319 ²²
<i>n</i> -Heptyl	$\text{CH}_3(\text{CH}_2)_6\text{Br}$	70	144–147 (12 mm.)	$\text{C}_{12}\text{H}_{21}\text{O}_2\text{N}$	6.57	6.70	1.4345 ²²
<i>n</i> -Octyl*	$\text{CH}_3(\text{CH}_2)_7\text{Br}$	75	159–162 (15 mm.)	$\text{C}_{13}\text{H}_{23}\text{O}_2\text{N}$	6.22	6.37	1.4381 ²²
<i>n</i> -Decyl	$\text{CH}_3(\text{CH}_2)_9\text{Br}$	65	148–150 (5 mm.)	$\text{C}_{15}\text{H}_{27}\text{O}_2\text{N}$	5.53	5.76	1.4429 ²²
2-Ethyl- <i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{Br}$	50	138–142 (19 mm.)	$\text{C}_{11}\text{H}_{19}\text{O}_2\text{N}$	7.10	7.26	1.4333 ²⁴
2-Ethyl- <i>n</i> -hexyl	$\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{Br}$	50	118–122 (4 mm.)	$\text{C}_{13}\text{H}_{23}\text{O}_2\text{N}$	6.22	6.50	1.4390 ²⁴
β -Phenylethyl	$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{Br}$	78	163–165 (7 mm.)	$\text{C}_{12}\text{H}_{15}\text{O}_2\text{N}$	6.45	6.55	1.5030 ¹⁶
γ -Phenylpropyl	$\text{C}_6\text{H}_5(\text{CH}_2)_3\text{Br}$	68	175–177 (10 mm.)	$\text{C}_{14}\text{H}_{17}\text{O}_2\text{N}$	6.05	6.17	1.4975 ²²
Cyclohexyl**	$\text{C}_6\text{H}_{11}\text{Br}$	23	125–127 (8 mm.)	—	—	—	1.4580 ²⁵
1-Methylnaphthyl	$\text{C}_{10}\text{H}_7\text{CH}_2\text{Cl}$	45	146–148 (0.005 mm.)	—	—	—	1.5690 ²⁴

* Ref. (7).

** Ref. (3).

The following α -amino acids were prepared in yields varying from 35 to 53%: *dl*- α -aminocaprylic acid, *dl*- α -aminopelargonic acid, *dl*- α -aminolauric acid, *dl*- α -(2-ethyl-*n*-butyl)- α -aminoacetic acid, *dl*- α -(2-ethyl-*n*-hexyl)- α -aminoacetic acid, *dl*- α -amino- γ -phenylbutyric acid, *dl*- α -amino- γ -benzylbutyric acid, *dl*-C-cyclohexylglycine and *dl*- α -amino- β -1-naphthylpropionic acid.

This result and those previously reported in the literature clearly indicate that the Darapsky method for the synthesis of α -amino acids is of wide application.

Experimental*

Substituted Cyanoacetic Esters (I)

To a solution of sodium ethoxide (400 ml. of absolute ethyl alcohol per mole of sodium) were added two equivalents of ethyl cyanoacetate and one equivalent of organic halide while cooling. The reaction mixture was boiled under reflux on a water bath until it was neutral to wet litmus paper. The alcohol was removed by distillation and the residue poured into cold water. The oily layer formed was decanted and the aqueous layer, previously acidified, was extracted several times with ether. The oily layer and the ethereal solutions were dried over anhydrous sodium sulphate, the ether evaporated, and the residue distilled under reduced pressure.

The properties and yields of the esters are summarized in Table I.

Substituted Cyanoacethydrazides (II)

The substituted cyanoacetates were stirred at room temperature with one equivalent of hydrazine hydrate (100%); heat was evolved. The reaction mixtures were allowed to stand in an evacuated desiccator over phosphorus pentoxide to eliminate the alcohol formed. Most of the hydrazides solidified and were crystallized from ethanol. Their properties are given in Table II.

TABLE II
 α -SUBSTITUTED CYANOACETHYDRAZIDES, $\text{RCH}(\text{CN})\text{CONHNH}_2$

R	M.p., ° C.	Formula	Nitrogen, %	
			Calc.	Found
<i>n</i> -Hexyl	69-70	$\text{C}_9\text{H}_{17}\text{ON}_2$	22.93	23.03
<i>n</i> -Heptyl	89-90	$\text{C}_{10}\text{H}_{19}\text{ON}_2$	21.30	21.57
<i>n</i> -Octyl	80-81	$\text{C}_{11}\text{H}_{21}\text{ON}_2$	19.88	19.99
<i>n</i> -Decyl	89-90	$\text{C}_{13}\text{H}_{25}\text{ON}_2$	17.56	17.32
β -Phenylethyl	90-91	$\text{C}_{11}\text{H}_{13}\text{ON}_2$	20.67	20.62
γ -Phenylpropyl	89-90	$\text{C}_{12}\text{H}_{15}\text{ON}_2$	19.34	19.25

* All melting points are uncorrected.

Derivatives of Substituted Cyanoacethydrazides

All the hydrazides were identified by their condensation products with anisaldehyde, benzaldehyde, or acetone. The properties of the derivatives are listed in Table III.

TABLE III
ANISAL, BENZAL, AND ISOPROPYLIDENE DERIVATIVES

Compound	M.p., ° C.	Formula	Nitrogen, %	
			Calc.	Found
$\text{RCH(CN)CONHN=CHC}_6\text{H}_4\text{OCH}_3$ R = <i>n</i> -Hexyl	109–110	$\text{C}_{17}\text{H}_{25}\text{O}_2\text{N}_3$	13.94	13.69
<i>n</i> -Heptyl	106–108	$\text{C}_{18}\text{H}_{27}\text{O}_2\text{N}_3$	13.32	13.51
<i>n</i> -Octyl	105–106	$\text{C}_{19}\text{H}_{29}\text{O}_2\text{N}_3$	12.75	12.82
<i>n</i> -Decyl	109–110	$\text{C}_{21}\text{H}_{31}\text{O}_2\text{N}_3$	11.76	11.92
2-Ethyl- <i>n</i> -butyl	130–131	$\text{C}_{17}\text{H}_{25}\text{O}_2\text{N}_3$	13.94	14.00
2-Ethyl- <i>n</i> -hexyl	89– 90	$\text{C}_{19}\text{H}_{27}\text{O}_2\text{N}_3$	12.75	12.77
β -Phenylethyl	145–147	$\text{C}_{18}\text{H}_{19}\text{O}_2\text{N}_3$	13.07	13.01
γ -Phenylpropyl	129–130	$\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}_3$	12.53	12.49
Cyclohexyl	178–180	$\text{C}_{17}\text{H}_{21}\text{O}_2\text{N}_3$	14.03	14.19
1-Methylnaphthyl	174–175	$\text{C}_{22}\text{H}_{19}\text{O}_2\text{N}_3$	11.72	11.42
$\text{RCH(CN)CONHN=CHC}_6\text{H}_5$ R = <i>n</i> -Hexyl	72– 73	$\text{C}_{16}\text{H}_{21}\text{ON}_3$	15.52	15.60
<i>n</i> -Heptyl	81– 82	$\text{C}_{17}\text{H}_{23}\text{ON}_3$	14.73	14.67
<i>n</i> -Octyl	70– 71	—	—	—
2-Ethyl- <i>n</i> -butyl	87– 88	—	—	—
β -Phenylethyl	129–130	$\text{C}_{18}\text{H}_{17}\text{ON}_3$	14.94	14.77
$\text{RCH(CN)CONHN=C(CH}_3)_2$ R = <i>n</i> -Heptyl	80– 81	$\text{C}_{18}\text{H}_{25}\text{ON}_3$	17.70	17.72

Amino Acids (V)

The substituted cyanoacethydrazides were transformed into the azides as originally outlined by Darapsky (1). The aqueous suspensions of the hydrazides were treated in the cold with nitrous acid and the azides extracted with ether. To the ethereal solutions, ethanol was added. The ether was evaporated and the resulting alcoholic solutions refluxed for about one hour. After the removal of the alcohol, the crude urethanes were obtained as pale or dark brown liquids.

The urethanes were hydrolyzed with two different agents: hydrochloric acid (20%) or a mixture of equal volumes of concentrated hydrochloric acid, formic acid (85%), and water. The amino acids were isolated by neutralizing, with dilute ammonia, solutions in water of their purified hydrochlorides.

The properties and yields of the amino acids together with the properties of their derivatives are given in Table IV.

TABLE IV
AMINO ACIDS AND DERIVATIVES

Compound	Hydrolyzing agent	Time, hr.	Yield, %	Derivative	M.p., ° C.	Formula	Nitrogen, %	
							Calc.	Found
<i>dl</i> - α -aminocaprylic acid	20% HCl	84	35	hydantoin	147-148	C ₈ H ₁₅ O ₂ N ₂	15.20	15.28
<i>dl</i> - α -aminopelargonic acid	20% HCl	85	47	hydantoin	142	C ₁₀ H ₁₇ O ₂ N ₂	14.13	14.48
<i>dl</i> - α -aminocapric acid	20% HCl	88	53	phenylureido	128-129	C ₁₇ H ₂₅ O ₂ N ₂	9.14	9.33
<i>dl</i> - α -aminolauric acid	mixed acids	69	41	phenylureido	127-128	C ₁₉ H ₂₇ O ₂ N ₂	8.38	8.51
<i>dl</i> - α -(2-ethyl- <i>n</i> -butyl)- α -aminoacetic acid	20% HCl	108	34	phenylureido*	131-132	C ₁₈ H ₂₇ O ₂ N ₂	10.06	10.24
<i>dl</i> - α -(2-ethyl- <i>n</i> -hexyl)- α -aminoacetic acid	20% HCl	108	40	hydantoin**	123-124	C ₂₁ H ₃₃ O ₂ N ₂	13.19	13.34
<i>dl</i> - α -amino- γ -phenylbutyric acid	mixed acids	24	34	hydantoin†	167-168	C ₁₁ H ₁₇ O ₂ N ₂	13.71	13.97
<i>dl</i> - α -amino- γ -benzylbutyric acid	20% HCl	84	38	hydantoin	158-159	C ₁₂ H ₁₇ O ₂ N ₂	12.83	12.98
<i>dl</i> -C-cyclohexylglycine	20% HCl	48	45	phenylureido	190	C ₁₄ H ₂₃ O ₂ N ₂	10.14	10.31
<i>dl</i> - α -amino- β -1-naphthylpropionic acid	20% HCl	68	20	phenylureido	145-146	C ₂₀ H ₁₉ O ₂ N ₂	8.38	8.64

* Hydantoin, *m.p.* 189° C.** Phenylureido, *m.p.* 129-130° C.† Phenylureido, *m.p.* 173° C.

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VARIATIONS DES TENEURS EN GLYCOGÈNE ET EN TRÉHALOSE PENDANT LE SÉCHAGE DE LA LEVURE¹

PAR ROGER PAYEN

Sommaire

La transformation des glucides de la levure pendant sa dessiccation a été étudiée. Une méthode de dosage du glycogène est proposée, dans laquelle l'alcool méthylique remplace l'alcool éthylique pour la précipitation. Pendant le séchage de la levure, la teneur en glucides totaux de la cellule change peu, alors que le glycogène disparaît presque complètement. Il semble que du tréhalose, formé pendant la dessiccation de la levure, prend la place du glycogène.

Introduction

Le but du présent travail était d'étudier les variations dans la teneur en glucides se produisant pendant le séchage de la levure préparée spécialement pour l'obtention des levures sèches vivantes de boulangerie.

Les principaux constituants glucidiques de la levure sont le glycogène (1), la gomme de levure ou mannane (7), le tréhalose (10), et un polyose, le glucane-1,3 (3, 11). Des méthodes de dosage pour le glycogène (3, 4, 5, 9), la mannane (2, 4, 9) et le tréhalose (8, 10), ont été proposées, mais elles laissent toutes plus ou moins à désirer.

Les procédés actuels d'extraction des glucides de la levure avec de l'hydroxyde de potassium à 60-85%, suivie d'une précipitation de l'extrait par l'alcool éthylique, donnent un mélange contenant au moins la gomme de levure et le glycogène. Deux méthodes ont été suggérées pour estimer séparément ces deux constituants. La première, due à Mayer (5), sépare le glycogène d'avec la mannane en saturant la solution contenant les deux glucides par le sulfate d'ammonium, ce qui précipite le glycogène. La deuxième méthode précipite la mannane sous forme de complexe cuivrique, au moyen de la liqueur de Fehling. Cette dernière méthode a été utilisée par Ling, Nangi et Paton (4), Hashitani (2), puis perfectionnée par Stockhausen et Silbereisen en 1935 (9). Le glycogène et la mannane ainsi séparés sont ensuite hydrolysés par un acide et les sucres réducteurs dosés.

Les méthodes de dosage du tréhalose consistent soit à extraire la levure par l'alcool à 90%, puis à laisser cristalliser l'extrait (10), soit à extraire la levure avec une solution normale d'acide sulfurique (8) ou avec de l'alcool à 90% et à doser les sucres réducteurs présents après hydrolyse acide de l'extrait.

Résultats expérimentaux

Dosage du glycogène

Au cours de nos recherches, nous avons eu l'occasion de comparer les résultats obtenus en dosant le glycogène de la levure par la méthode de

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Stockhausen (9), avec ceux que donne la méthode colorimétrique à l'iode (6). La différence très grande obtenue entre les valeurs trouvées par les deux méthodes dépasse de beaucoup les erreurs possibles d'analyse.

TABLEAU I
TENEURS EN GLYCOGÈNE OBTENUES PAR DEUX
MÉTHODES DIFFÉRENTES

Levure N°	Méthode Stockhausen, %	Méthode colorimétrique, %
19 pressée	16.36	7.0
30 séchée	6.51	0.4
31 "	9.77	0.8
33 "	7.78	1.0
41 "	14.16	2.0

La méthode Stockhausen consiste à précipiter le glycogène de sa solution alcaline en amenant celle-ci à une concentration d'environ 75% en alcool éthylique. Nous avons constaté que la quantité de glycogène obtenue par cette méthode diminue beaucoup, si l'on reprécipite le glycogène une deuxième fois.

TABLEAU II
VARIATION DE LA TENEUR EN GLYCOGÈNE AVEC LE
NOMBRE DE PRÉCIPITATIONS

Levure N°	Glycogène après une précipitation, %	Glycogène après deux précipitations, %
41	14.16	6.98

L'alcool méthylique précipite également le glycogène quantitativement de ses solutions alcalines, quand on en utilise deux volumes pour un de solution. Ainsi, des dosages de glycogène sur des foies d'animaux ont donné les résultats suivants:

TABLEAU III
COMPARAISON ENTRE L'ALCOOL MÉTHYLIQUE ET L'ALCOOL ÉTHYLIQUE COMME
AGENT DE PRÉCIPITATION DU GLYCOGÈNE

Source du glycogène	Glycogène précipité par l'alcool éthylique (1 précipitation), %	Glycogène précipité par l'alcool méthylique (1 précipitation), %
Foie de rat (Traité immédiatement après la mort de l'animal)	2.37	2.40
Foie de veau (Conservé à la glacière)	0.48	0.45

Nous avons également traité un extrait alcalin de levure au moyen de deux volumes d'alcool méthylique. Le précipité obtenu a été séparé par filtration, et le filtrat distillé en partie afin de le débarrasser de l'alcool méthylique. Le résidu, additionné d'alcool éthylique, donne un précipité qui ne contient pas de glycogène ni de mannane, comme le montrent l'absence de coloration par l'iode et l'absence de précipité quand on sature la solution avec du sulfate d'ammonium ou qu'on lui ajoute de la liqueur de Fehling.

Nous avons donc modifié la méthode proposée par Stockhausen et nous décrivons notre méthode à la fin de ce travail.

L'analyse de différentes levures pressées ou séchées, obtenue en utilisant l'alcool méthylique, est donnée dans le tableau IV, à côté des résultats donnés par la méthode utilisant l'alcool éthylique.

TABLEAU IV
TENEURS EN GLYCOGÈNE OBTENUES EN CHANGEANT
L'AGENT DE PRÉCIPITATION

Levure N°	Glycogène précipité par l'alcool éthylique, %	Glycogène précipité par l'alcool méthylique, %
19 pressée	16.36	6.18
20 "	13.95	8.14
30 séchée	6.51	0.93
31 "	9.77	2.25
33 "	7.78	2.49
41 "	14.16	3.23

La différence entre les résultats obtenus par les deux méthodes représente un glucide différent du glycogène et de la mannane. Comme les conditions de précipitation du glycogène par trois volumes d'alcool éthylique dans la méthode Stockhausen pourraient favoriser la cristallisation du tréhalose, qui dans certaines levures représente jusqu'à 18% de la matière sèche, ce qui expliquerait les chiffres trop élevés obtenus pour le glycogène, nous avons fait des expériences avec des mélanges de glycogène pur et de tréhalose. Ces expériences démontrent que le tréhalose ne se sépare pas avec le glycogène, pendant la précipitation de ce dernier par la méthode de Stockhausen.

1° expérience. 0.075 g. de glycogène + 0.1125 g. de tréhalose; trouvé 0.077 g. de glycogène.

2° expérience. 0.060 g. de glycogène + 0.1260 g. de tréhalose; trouvé 0.054 g. de glycogène.

Les quantités de tréhalose ajoutées dans ces essais correspondaient à des teneurs respectives de 15 et 17% en tréhalose dans la levure.

La préparation de la levure sèche vivante pour la boulangerie, à partir de levures cultivées spécialement dans ce but, est accompagnée d'une diminution très marquée de la teneur en glycogène, telle que mesurée par notre méthode de dosage.

TABLEAU V
VARIATION DE LA TENEUR EN GLYCOGÈNE PENDANT
LA DESSICCATION

Levure N°	Glycogène avant séchage, %	Glycogène après séchage, %
19	6.18	1.21
20	8.14	2.76
21	4.86	1.55

En général, du reste, les levures séchées ont toujours une teneur en glycogène très faible (voir tableau I).

D'autre part, la teneur en glucides totaux de la levure ne diminue pratiquement pas pendant le séchage. Il en est de même pour la teneur en glucides autofermentescibles de la cellule.

TABLEAU VI
VARIATION DE LA TENEUR EN GLUCIDES DE LA LEVURE
PENDANT LA DESSICCATION

Levure N°	Avant séchage, %	Après séchage, %
<i>Glucides totaux*</i>		
20	36.74	36.20
21	36.32	35.43
30	29.44	29.90
43	24.13	24.60
<i>Glucides autofermentescibles*</i>		
21	18.49	17.81

**Calculés en glucose.*

La perte en glycogène observée après dessiccation de la levure doit donc être en partie compensée par la formation d'un autre glucide dans la cellule, et il semble en effet que du tréhalose prend naissance en quantité à peu près équivalente au glycogène disparu.

Dosage du tréhalose

Pour doser le tréhalose, nous avons extrait la levure pressée ou séchée par l'alcool à 90% au reflux. L'extrait alcoolique était ensuite mis à cristalliser. La cristallisation quantitative du tréhalose est incertaine, mais cette méthode donne au moins la certitude que les valeurs obtenues se rapportent au glucide étudié. Il est remarquable que les levures sèches vivantes contiennent toutes plus de tréhalose que les levures pressées.

TABLEAU VII
TENEUR EN TRÉHALOSE DE LA LEVURE DE BOULANGERIE

Levure N°	Tréhalose, %	Levure N°	Tréhalose, %
22 pressée	3.6	31 séchée	8.6
27 "	3.5	33 "	7.8
20 séchée	6.8	39 "	6.2
30 "	5.8	41 "	18.0

Des levures,* étudiées avant et après séchage, ont donné les résultats suivants.

TABLEAU VIII
VARIATION DES TENEURS EN GLUCIDES DE LA LEVURE PENDANT LA DESSICCATION

Levure N°	Glucides étudiés	Avant séchage, %	Après séchage, %
20	{ Glucides totaux	36.74	36.20
	{ Glycogène	8.14	2.76
	{ Tréhalose	2.50	6.50
21	{ Glucides totaux	36.32	35.43
	{ Glucides autofermentescibles	18.49	17.81
	{ Glycogène	4.86	1.55
	{ Tréhalose	3.50	6.70

Conclusions

La levure de boulangerie préparée spécialement pour la fabrication des levures sèches vivantes perd, pendant la dessiccation, la majeure partie de son glycogène. Toutefois, du tréhalose prend naissance pendant le séchage de la levure si bien que la teneur en glucides totaux ne diminue presque pas.

Méthodes d'Analyse

1. Dosage des glucides donnant un sucre réducteur après hydrolyse acide

Placer 1.5 g. de levure sèche et 5 ml. d'eau, ou bien 5 g. de levure pressée, dans une fiole conique de 125 ml. Ajouter 10 ml. d'acide chlorhydrique concentré et 70 ml. d'eau. Tenir au bain-marie bouillant, sous reflux, pendant trois heures. Refroidir. Neutraliser par la soude caustique, en présence de phénolphthaléine, en refroidissant, et en évitant tout excès d'alcali, puis décolorer par quelques gouttes d'acide acétique.

Déféquer la solution en ajoutant 10 ml. d'une solution saturée d'acétate neutre de plomb, diluer à 100 ml. exactement puis laisser déposer quelques heures.

* Levure cultivée dans les laboratoires de l'Université de Montréal à partir de la levure pressée de boulangerie commerciale F. A. Lallemand.

Filtrer sur papier Whatman N° 40. Prélever 50 ml. du filtrat, dans un flacon jaugé de 100 ml. Ajouter 10 ml. d'une solution saturée d'oxalate de potassium, compléter à 100 ml., puis filtrer.

Prélever 50 ml. du filtrat pour le dosage des sucres réducteurs d'après la méthode de Munson et de Walker.

2. Dosage des glucides autofermentescibles

Placer dans une fiole conique de 125 ml., 5 g. de levure pressée ou 1.5 g. de levure séchée avec 15 ml. d'eau distillée et 2 à 3 ml. d'éther éthylique. La levure est laissée en contact 48 h. en renouvelant l'éther si nécessaire, puis elle est ensuite hydrolysée et les sucres réducteurs non fermentés dosés d'après la méthode I.

La différence entre les sucres réducteurs trouvés par la méthode I et ceux après autofermentation représente les glucides autofermentescibles.

3. Dosage du glycogène après hydrolyse acide

Dans une fiole conique de 250 ml., on place 6 g. de levure sèche et 14 ml. d'eau, ou 20 g. de levure pressée. On ajoute 60 ml. d'une solution d'hydroxyde de potassium (65 g. d'hydroxyde de potassium avec 35 ml. d'eau). On met à refluer, très doucement au début, pendant trois heures.

Le mélange est refroidi, dilué exactement à 100 ml., puis additionné d'un peu de terre à diatomées. On filtre sur papier Reeve Angel N° 202, en couvrant l'entonnoir et le flacon receveur afin de diminuer l'évaporation.

On prélève une portion de 50 ml., dans laquelle on précipite la gomme et le glycogène par 100 ml. d'alcool méthylique et un cristal d'acétate de sodium. Il précipite immédiatement des grumeaux blancs. On laisse reposer une nuit, puis le précipité est décanté sur un papier filtre Whatman N° 40. On lave trois fois le précipité avec de l'alcool méthylique à 75% contenant un peu d'acétate de sodium.

Le précipité est ensuite dissous dans une solution d'hydroxyde de potassium à 2% chaude, et le papier filtre lavé également avec la solution alcaline à 2%. On dilue à 100 ml. dans un flacon jaugé. (Solution A).

(a) Dosage de la gomme et du glycogène

Prélever exactement 50 ml. de la solution A, ajouter 9 ml. d'acide chlorhydrique concentré et 21 ml. d'eau. Tenir sous reflux, au bain-marie pendant trois heures. Refroidir et continuer comme pour le dosage des glucides tel que décrit dans la méthode I.

(b) Dosage de la gomme

Prélever 40 ml. de la solution A, puis ajouter 80 ml. de liqueur de Fehling froide, tel que décrit par Stockhausen et Silbereisen (9). Filtrer sur papier

Whatman N° 40, après avoir laissé reposer pendant une nuit, et laver avec une solution d'hydroxyde de potassium à 2%.

Dissoudre le résidu avec un mélange de 9 ml. d'acide chlorhydrique concentré et 71 ml. d'eau. Hydrolyser au bain-marie sous reflux pendant trois heures. Procéder ensuite au dosage des sucres réducteurs tel que décrit pour la méthode I.

L'équivalent-glucose du glycogène est calculé par différence; on obtient la valeur exacte en glycogène en multipliant par le facteur 0.927 (9).

4. Dosage colorimétrique du glycogène

On utilise 20 ml. de l'extrait alcalin tel qu'obtenu par digestion de la levure avec la solution concentrée d'hydroxyde de potassium (voir méthode I).

Le glycogène, avec d'autres glucides, est précipité à deux reprises, par trois volumes d'alcool éthylique et un peu d'acétate de sodium.

On dissout le précipité dans 20 ml. d'eau distillée, on acidifie avec un peu d'acide chlorhydrique, et on ajoute 10 gouttes d'une solution d'iode décinormale. La coloration brune produite est comparée avec celle donnée par un poids connu de glycogène pur.

5. Dosage du tréhalose

On place 25 g. de levure sèche dans un extracteur Soxhlet modifié, surmonté d'un premier réfrigérant sec servant de réchauffeur et d'un deuxième réfrigérant dans lequel circule l'eau de condensation. On fait refluer avec 100 ml. d'alcool à 80% pendant 15 h. environ.

Le contenu du ballon d'extraction est refroidi afin de précipiter des substances gommeuses jaunâtres (A), puis la solution alcoolique décantée, ajustée à une concentration d'alcool de 90% environ est mise à la glacière pendant une semaine.

Le résidu gommeux (A) précipité est extrait de nouveau sous reflux pendant quelques heures par de l'alcool à 90% afin d'enlever le tréhalose entraîné, puis la solution refroidie et décantée, est également placée à la glacière pendant une semaine. Après ce temps les cristaux sont recueillis, lavés à l'alcool à 90% froid, puis par de l'éther. Ils sont ensuite séchés rapidement à l'air.

Pour les levures pressées, l'extraction du tréhalose est plus difficile. On prend 100 g. de levure pressée et on ajoute assez d'alcool à 95% pour avoir une solution d'alcool à 90%. On fait refluer plusieurs heures et on filtre. Le résidu est repris de nouveau par l'alcool à 90%. Les extraits combinés sont distillés sur bain-marie, puis le résidu gommeux est extrait à deux reprises sous reflux par l'alcool éthylique à 90% bouillant. On met à cristalliser ensuite comme pour la levure séchée.

Dans les deux cas, il faut ajouter un facteur de correction correspondant à la solubilité du tréhalose dans l'alcool à la température de cristallisation.

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THE EXTRACTION AND PURIFICATION OF XENON AND KRYPTON ISOTOPES FROM NEUTRON IRRADIATED URANIUM¹

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Abstract

Both long-lived and stable isotopes of krypton and xenon are formed as the result of the slow neutron fission of uranium 235. A method is described for the extraction of these gases from massive neutron irradiated uranium metal, for separating them from contaminating gases and from each other and measuring them in a McLeod gauge, the amounts of uranium being of the order of 50 gm. and the rare gases of the order of 10^{-3} cc. at N.T.P. An accurate value of the ratio of fission xenon to fission krypton is given. Further experiments concern Geiger-Müller counter measurements on the long-lived krypton isotope.

Introduction

As long-lived or stable xenon isotopes were known to occur in, or at the end of, several fission chains, a program was initiated to extract, purify, and examine macro quantities of xenon gas from pile irradiated uranium. The mass spectrometric examination of the final samples has already been reported on by Thode and Graham (3).

It was expected that samples of the order of 10^{-3} cc. at N.T.P. would be obtained from 30 to 50 gm. of the uranium available. Argon, probably occluded during the preparation of the metal, was found to be present in the extracted gases in considerable quantity. Preliminary tests by Thode and Graham indicated that argon, krypton, and xenon were all present, and also a mass 85—presumably a long-lived krypton isomeric with 4.0 hr. krypton 85.

A program was then initiated to extract all the rare gases, separate the argon, xenon, and krypton fractions, estimate them individually to $\pm 0.5\%$, examine them for long-lived radioactive isotopes, and submit them to mass spectrometric examination (3).

Experimental

Specimens of pure uranium metal were prepared in the form of disks about 1.1 in. in diameter, weighing between 20 and 50 gm. Twenty disks were made up into a cylindrical composite "slug", which was sealed into an aluminum sheath and pile irradiated. In order to avoid unnecessary handling of the disks after irradiation (because even after six months they were still appreciably radioactive) the disks were all weighed before irradiation and their weights stamped on them with punches. About 15 disks were kept unirradiated for blank experiments.

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Massive uranium metal was found to dissolve in a controllable manner in saturated potassium cuprichloride solution with the evolution of some hydrogen which was sufficient to act as a convenient carrier for sweeping the rare gases through the drying train. The gas extraction apparatus is shown in Fig. 1.

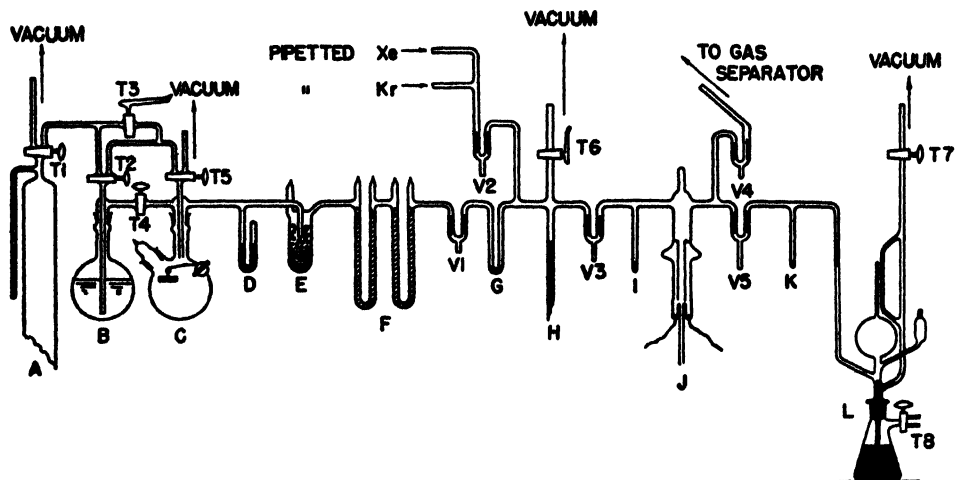


FIG. 1. Gas extraction apparatus.

Vessels *B* and *C* were of 1 liter capacity, and about 600 cc. of a saturated potassium cuprichloride solution in *B* was swept clean of dissolved air with pure hydrogen from reservoir *A* passing through *T*₁, *T*₂, *T*₄, and *T*₅ to vacuum. The solution was then transferred to the evacuated reaction vessel *C* through *T*₂ and *T*₅. A platinum wire basket was suspended from a rotating arm in *C* whose movement could be controlled from outside the vacuum system through a greased cone and socket joint. This basket containing the uranium metal specimen could thus be lowered into the solution and, if the reaction became too vigorous or if the manometers *D* and *H* indicated too high pressure in the system, hoisted out again.

The gas mixture from the uranium dissolution consisted of a relatively large amount of hydrogen and water vapor, traces of hydrocarbons from uranium carbides, and the small amounts of rare gases. This mixture passed through a rough drying trap, *E*, containing pellets of solid potassium hydroxide, through two U-tubes, *F*, of anhydrous magnesium perchlorate and finally through a charcoal trap, *G*, cooled in liquid air, where all the gases were adsorbed except hydrogen, which passed through and was pumped away through *T*₆. From this point onward where the gases had been separated from their carrier, they were manipulated by standard high vacuum technique in part of the apparatus in which mercury ventils (*V*₁–*V*₅) replaced stopcocks in order to avoid possible loss of xenon and krypton in grease.

By warming *G* and cooling the small charcoal tube, *I*, the mixture of hydrocarbons and rare gases (sometimes with some hydrogen) was transferred into a section of the apparatus containing a calcium furnace (Fig. 2) after the

original of Soddy (2), except that it was in a sealed Pyrex envelope completely free from grease. *A* was the calcium metal in a stainless steel thimble, *B*. A 90% Pt - 10% Rh flat filament, *D*, was wound into a spiral cut in a fused silica support, *C*. Leads to the furnace entered the envelope, *F*, through tungsten seals and were fitted to nickel tubes, *E*. The connections were made with tweezers through side tubes in the envelope, which were afterwards

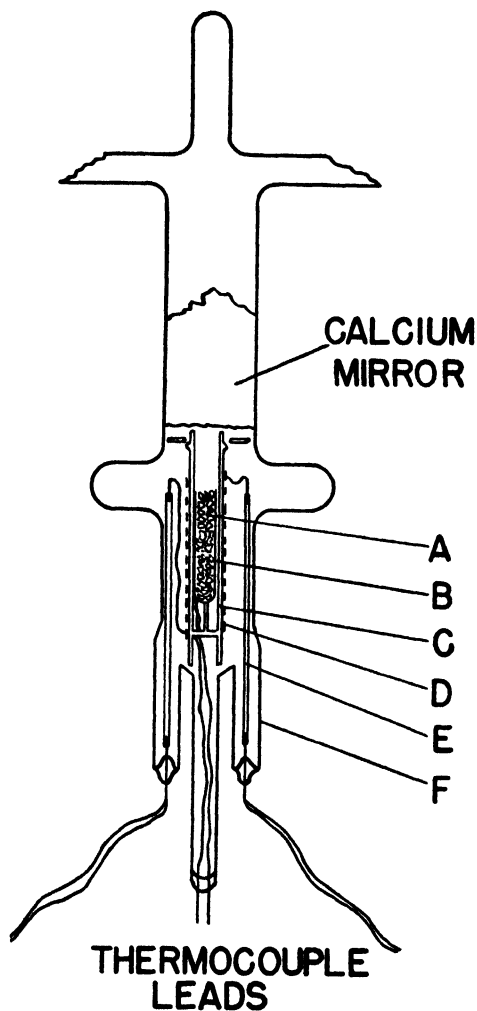


FIG. 2. Calcium furnace.

sealed off. The sealed-off tube on top of the furnace could be opened and a fresh charge of calcium metal introduced without remaking the furnace. The gas mixture was subjected to calcium vapor at temperatures between 450° and 500° C. for about 20 min. Calcium forms solid products with all gases except the rare gases, and after a time, which was usually about 20 to 30 min., the rare gases were shown spectroscopically to be free from hydrogen, hydrocarbon, or any other impurity. The gases were transferred to the McLeod gauge by adsorbing them in charcoal tube *K*.

Gas measurements were carried out in a McLeod gauge (Fig. 1, *L*) of special design. The capillaries were about 2.5 mm. I.D. and the closed capillary was calibrated with mercury. A small side bulb connected below the main bulb took off a sample of the contents of the McLeod gauge which could be contained in a capillary tube at the top, excited with a Tesla coil, and the spectrum examined. Absolute calibration of the McLeod gauge was carried out using measured quantities of krypton and xenon pipetted into the apparatus through V_2 at known temperature and pressure. Instead of tapping capillaries of the gauge by hand, these were vibrated by an electrically driven reed and the mercury levels were then measured using a travelling microscope. With these refinements an accuracy of $\pm 0.5\%$ was obtainable in the measurements of amounts of gas of not less than 0.5 cu. mm. at N.T.P.

Before the irradiated uranium was used, the apparatus was tested rigorously on samples of pure rare gases of the order of the amounts expected from fission. No losses were observed when samples of krypton and xenon were treated repeatedly with calcium vapor. This showed that the gases were not trapped in the mirror of calcium condensing out on the walls of the furnace. In other experiments, known amounts of argon, krypton, and xenon were condensed separately into a small charcoal tube sealed temporarily to the vessel in which the uranium was to be dissolved. The proposed extraction procedure was then followed, using a stream of pure hydrogen admitted through T_1 , T_3 , and T_5 in place of the hydrogen which would have been evolved during solution of the metal. In different experiments, widely different flow speeds of hydrogen were used, and in each case krypton and xenon were recovered quantitatively. Even in the case of the less condensable argon, the final amount recovered was within 1% of the original. Blank experiments on the hydrogen used showed no trace of rare gas, but, as has already been pointed out, blank experiments on unirradiated uranium showed the presence of argon.

Because of the occurrence of argon and krypton in the gas mixture extracted from irradiated uranium, it was desirable to have methods for their quantitative analysis. Estimates of the relative amounts of the gases could be made from mass spectroscopic data, but, as Thode and Graham point out (3), difficulties are involved owing to fractionation of small quantities of the gases in the fine capillary leak leading into the ion source of the instrument and also to differences in ionization potentials. It was therefore decided to carry out the direct separation of argon, krypton, and xenon and measurement of the fractions in the McLeod gauge.

For this purpose, a new section of apparatus was built communicating through a vent to the calcium furnace. It consisted of a fractional adsorption system of nine units, in many respects similar to one described by Dr. E. Glückauf* for the separation of helium and neon. The fact that argon, krypton, and xenon can all be adsorbed completely on charcoal at liquid

* The work of Glückauf was carried out in London in 1938, and, although not published in detail until 1946, was known to the authors in 1945.

nitrogen temperature made slight simplifications possible. U-tubes containing about 0.08 gm. of charcoal each and Toepler pumps with a contact volume of 70 cc. were used. For the separation of argon from krypton the charcoal temperature was that of solid carbon dioxide-acetone or about $-78^{\circ}\text{C}.$, and for the separation of krypton from xenon a charcoal temperature of $-20^{\circ}\text{C}.$ was used. Glückauf points out that in optimal conditions, and where the amounts of gases to be separated are similar, the number of operational cycles producing the most effective separation of any two gases should be about twice the number of adsorption units. In our apparatus, the conditions were not quite optimal, and it was found experimentally that a separation at $-78^{\circ}\text{C}.$ of 24 operations removed 95% of the argon from a ternary mixture without any krypton getting through. The remaining 5% of the argon, together with the krypton and xenon, was then returned to the first unit of the separator and separated again, using 27 operations. This removed altogether 99.95% of the argon, together with a known 1% of the krypton. The remaining krypton and xenon were now returned to the first unit of the separator and the charcoal temperature raised to $-20^{\circ}\text{C}.$ Twenty-four operations at this temperature separated 95% of the remaining krypton, and, with the 5% of krypton and 100% of the xenon returned to the first unit, a further 24 operations separated all but 0.25% of the krypton which was left in the xenon.

Before the separator was used on fission gases, it was tested thoroughly with known mixtures of argon, krypton, and xenon. Purity of the products was checked by their adsorption behavior over charcoal at different temperatures and mass spectrometrically by Thode and Graham.

Results

Samples of rare gases were extracted from disks from two slugs. The two slugs were irradiated separately and under slightly different conditions. The results are given in Table I.

TABLE I

VOLUMES OF ARGON, KRYPTON, AND XENON IN SAMPLES OF URANIUM

Sample	Wt., gm.	Vol. of gas $\times 10^{-3}$ cc. at N.T.P.	Vol. $\times 10^{-3}$ cc. at N.T.P./gm. U
Specimen A	48.2	A: 2.80 Kr: 0.31 Xe: 1.56	A: 5.81 Kr: 0.64 Xe: 3.24
Specimen B	135.4	A: 3.03 Kr: 1.03 Xe: 5.22	A: 2.24 Kr: 0.76 Xe: 3.85

The ratios of total xenon to total krypton for specimens A and B are 5.03 and 5.07 respectively.

In Tables III and IV of their paper, Thode and Graham (3) summarize the abundance data for isotopes of xenon and krypton respectively. If the figure of 5.05 is taken as the ratio of xenon to krypton, we can tabulate the relative fission yields of masses 83, 84, 85, 86, 131, 132, 134, and 136, that of xenon 134 being taken as standard (Table II).

TABLE II
RELATIVE FISSION YIELDS

Mass No.	Relative fission yield	Mass No.	Relative fission yield
83	0.0779	131	0.381
84	0.148	132	0.566
85	0.0390	134	1.000
86	0.286	136	0.829

For the investigation of krypton for radioactivity a Geiger-Müller counter was constructed such that a small specimen of krypton could be mixed with the filling of argon and alcohol. A volume of 1.7×10^{-4} cc. at N.T.P. of fission krypton was put into a pipette that delivered a fraction 1/1056 to the counter. When this was mixed with the filling, a count of 27,600 per minute was obtained. This showed that at any rate one of the krypton isotopes must be radioactive, and because of the age of the uranium specimen, long lived. This is now believed to be krypton 85*, an isomer of the 4.0 hr. krypton 85.

Taking the percentage of krypton 85 to total krypton in the sample as 7.43%, and further assuming that every disintegration occurring within the cathode of the counter was counted, a specific activity for krypton 85 could be calculated giving the half life of the isotope. Using this technique the half life was estimated to be of the order of 16 years; Thode and Graham (3) obtained a more accurate estimate of 9.4 ± 0.4 years from a study of the decrease of the relative abundance of mass 85 in a specimen of fission krypton over a decay period of 440 days. The discrepancy in the estimated half lives is almost certainly due to counting inefficiency associated with the high counting rate used. A repetition of the experiment with a smaller amount of krypton would have provided presumably a value closer to that of Thode and Graham.

A similar experiment with fission xenon failed to give any conclusive evidence of the existence of a long-lived active xenon isotope.

Acknowledgment

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appreciation of the co-operation of Professor Thode and Mr. Graham by whose mass spectrometric technique so much information was obtained from such small gas samples.

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A PRELIMINARY STUDY OF THE PERMEABILITY OF CELLOPHANE TO LIQUIDS¹

By S. MADRAS,² R. L. McINTOSH,³ AND S. G. MASON

Abstract

The permeability of swollen cellophane accommodated by solvent exchange to a variety of liquid permeants has been studied. The degree of swelling, as measured by the thickness, has been shown to be retained when the swelling agent is removed by solvent exchange. Progressive swelling causes a controllable increase in the permeability to a given liquid, but the permeability coefficient at a given thickness is specific for the liquid. For water and aqueous solutions, K is about five times that of organic permeants. Values for the organic liquids are all of the same order of magnitude and show systematic variation with the degree of swelling. For homologous series of alcohols and ketones, K decreases with increasing chain length. Attempts to calculate the effective pore radius and pore number from K and the void fraction were successful only for water and dilute sodium hydroxide solutions, where a radius of 1.5×10^{-7} cm. and a pore number of 10^{13} per cm.³ were obtained. An independent method based on combined permeability and electrical conductance yielded a value of 3×10^{-7} cm. for the effective pore radius. With organic permeants, it is believed that complications introduced by swelling invalidate the application of the equations. The results obtained can be explained on the basis of viscous flow of the liquids through a porous network in which the number and dimensions of the pores vary with the degree of swelling, but evidence in favor of the validity of this mechanism is inconclusive.

Introduction

Cellophane possesses a number of properties that render it useful as a semi-permeable membrane and it has as a result found increasing application in ultrafiltration (13), dialysis (11), and osmometry (3, 14). Several brief investigations of the microstructure of cellophane materials have been carried out and have served to throw light on the mechanism of liquid permeability. It has been concluded from these studies that a Poiseuille type of viscous flow through a porous network occurs (17). McBain and Kistler (8) showed that the liquid permeability could be increased by swelling in water, and that a substantial portion of this increase could be retained after the water was removed by solvent exchange. Morton (13) showed that a further increase was obtained by swelling in solutions of sodium hydroxide.

This communication deals with a preliminary study of the permeability of cellophane to various liquids, including a number commonly used as solvents in osmotic pressure measurements, and the relation of permeability to the degree of swelling. Attempts were made to estimate the effective size of capillaries under various conditions of swelling from the permeability coefficient, the void fraction, and the measured thickness of swollen cellophane membranes, following a method originally used by Bechhold (1) and subsequently developed by other workers for collodion membranes (5). A partially

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independent, method based on permeability and electrical conductivity measurements using aqueous permeants was employed as a check on the validity of this method and was found to give substantially different results. These are subsequently referred to as the permeability - void volume and permeability-conductance methods and are described briefly below.

Permeability - Void Volume Method

The volume of viscous flow Q in unit time through unit cross section of a porous material of thickness L under a pressure gradient Δp may be expressed as

$$Q = P\Delta p = \frac{K\Delta p}{\eta L}, \quad (1)$$

where η is the viscosity of the permeant, and P and K respectively the permeability and the permeability coefficient of the porous medium.

If the capillary structure and the laws governing flow through a single capillary are known, K can in principle be predicted.

A generalized expression for K is given by the Kozeny-Carman equation (16) which for our purposes is most conveniently expressed in the form:—

$$m = \sqrt{\frac{k_0 K}{\epsilon \cos^2 \theta}} = \sqrt{\frac{k \cdot K}{\epsilon}}. \quad (2)$$

In this equation m is the mean hydraulic radius $\left(\frac{\text{wetted area}}{\text{wetted perimeter}} \right)$ of the pores in the capillary structure, k_0 is a shape factor determined by the geometry of the pores, and ϵ is the fractional void volume available for liquid flow. $\overline{\cos^2 \theta}$ is averaged over all pore orientations between the direction of the pore and the direction of macroscopic flow of the liquid.

It is evident from Equation (2) that prior knowledge of the capillary structure is necessary before the appropriate value of k can be selected. For this reason, permeability measurements alone will not reveal details of structure but can merely serve for the calculation of equivalent pore dimensions in terms of an assumed model. In practice k varies from 2 to 6 between the extreme cases of (a) a network of identical cylindrical capillaries parallel to the direction of macroscopic flow and (b) the interstices between cylinders at right angles to the direction of macroscopic flow (16). Despite the marked parallel alignment of the molecular chains in a sheet of cellophane, which would tend to favor model (b), we consider the simple model (a).

For unrestricted Poiseuille flow through a network of N independent cylindrical capillaries per unit area arranged parallel to the direction of macroscopic flow and of equal radius r ,

$$\left. \begin{aligned} K &= \frac{\pi r^4 N}{8} \\ \epsilon &= \pi r^2 N \end{aligned} \right\}. \quad (3)$$

Combining these equations, we obtain

$$r = 2m = \sqrt{\frac{8K}{\epsilon}} \quad (4)$$

and

$$N = \frac{\epsilon^2}{8\pi K}. \quad (5)$$

Equation (4) has been used extensively to compute the pore size of collodion membranes (5). Manegold and Viets (11) and Morton (13) applied it to regenerated cellulose membranes of the cellophane type.

In spite of the assumptions implied in deriving these equations, notably the oversimplified model of the capillary network rather than the more probable interconnecting web of tortuous pores of various size, the existence of Poiseuille flow unrestricted by electrokinetic and steric effects, and the assumption that the permeant is imbibed only in pores that are completely available for liquid flow, Elford and Ferry (4) concluded that the error in the average pore radius of collodion type membranes determined in this way should not exceed 25% provided r exceeds 10^{-6} cm.

Permeability-conductance Method

The determination of the permeability coefficient and the calculation of pore size by the above method depend on the knowledge of the void fraction and thickness of the membrane. Because of the peculiar swelling properties of cellophane a certain amount of doubt existed as to the validity of the measured values of these quantities. An alternative method that involves neither the thickness nor the void fraction of the membrane makes use of the electrical conductance corrected for surface conductance when the membrane is saturated with potassium chloride solutions of known concentration. Assuming a parallel-cylindrical network and that Ohm's law applies, we may write

$$C = \frac{\pi r^2 N \kappa}{L} \quad (6)$$

where κ is the specific conductivity of the permeant and C is the over-all conductance per unit area. Combining this relation with Equation (3) we obtain

$$r = \sqrt{\frac{8\eta \kappa P}{C}}. \quad (7)$$

A related method based simply on the measured conductance and void fraction has been used with some success on collodion membrane (7, 10).

Experimental Part

Materials

Canadian Industries Limited Cellophane grade No. 600 P.T. (not waterproofed) was used throughout this investigation. The thickness of the dry sheet was 0.004 cm.

All organic liquid permeants used were C.P. grade with the exception of ethanol and were further purified by a distillation. Absolute ethanol was prepared by the standard method using calcium oxide.

Potassium chloride solutions for the conductivity experiments were prepared from Reagent Grade potassium chloride and conductivity water of specific conductance less than 10^{-6} mho per cm.

Preparation of Membranes

The glycol plasticizer was removed from the cellophane by immersion in water at 60° C. for two hours. When degrees of swelling below that obtained in water were desired, 60% ethanol was substituted at this stage, and the thickness was adjusted by a further immersion for a period of at least 12 hr. in ethanol solutions of various concentrations. Typical results of the latter treatment are shown in Table I.

TABLE I
ADJUSTMENT OF MEMBRANE THICKNESS

Swelling solution		L , cm. $\times 10^3$
% Water	% Ethanol	
40	60	4.2 - 4.5
50	50	4.9 - 5.0
60	40	5.9 - 6.2
80	20	7.7 - 7.9
100	0	8.3 - 8.5

After this treatment, the membranes were washed with ethanol-water solutions of increasing ethanol content, in order to remove the water, and were then stored for at least four hours in absolute ethanol. This treatment did not decrease their thickness. They were then kept in anhydrous acetone until used. Prolonged storage in acetone was found to have no effect on the permeability or thickness of the membrane. With the exception of the washing stage this preparation was similar to that used by Carter and Record (3). Storage in ethanol and other alcohols was found to result in a gradual decrease in permeability.

Membranes intended for conductivity measurements were rinsed repeatedly in distilled water, after the plasticizer was removed by water immersion as described above. These membranes were stored in conductivity water, being transferred to their respective potassium chloride solutions at least 24 hr. before being used.

Highly swollen membranes were prepared by immersion of water-washed material in sodium hydroxide solutions. The sodium hydroxide was removed by repeated rinsing in distilled water until it could no longer be detected in

an ash test. The membranes were then stored in conductivity water, or in acetone after accommodation through successive alcohol washings as described above.

Permeability and Conductance Measurements

Most of the permeability measurements were carried out in brass cells similar in design to that of the Van Campen osmometer (2) modified to allow operation in permeability measurements in the same manner as with the combined permeability-conductance cell. The latter cell consisted (Fig. 1)

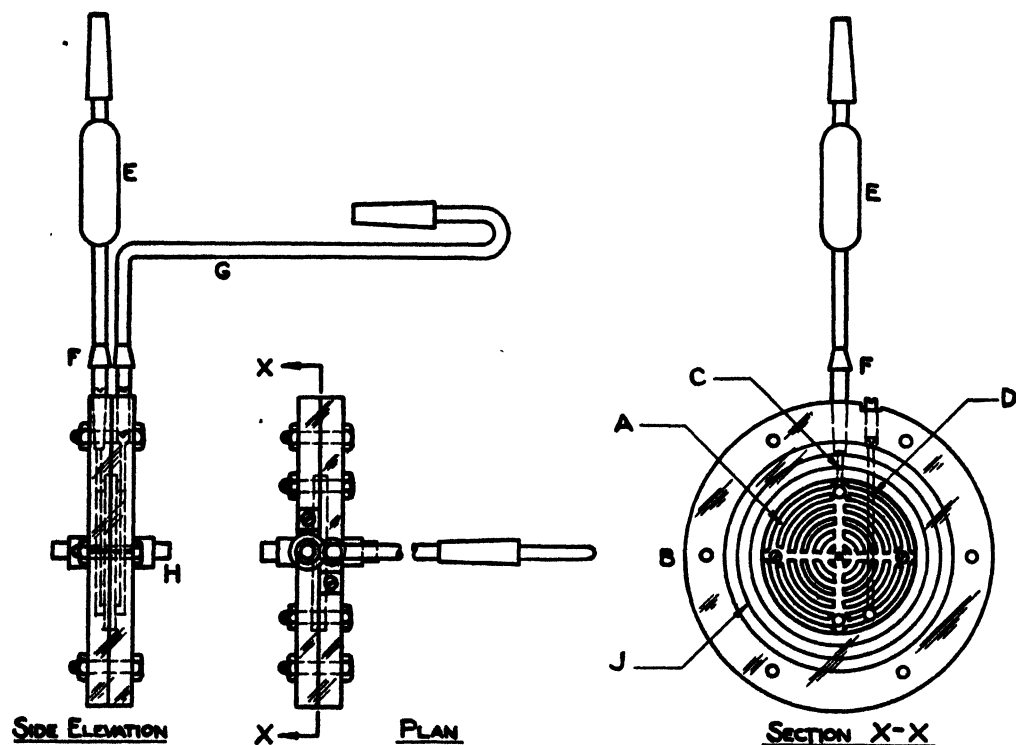


FIG. 1. The permeability-conductance cell.

of two machined Lucite half-cells between which the membrane was clamped by means of six symmetrically placed bolts. To obtain a leak-proof seal three concentric rings were cut into one of the half-cell faces to fit corresponding ridges on the face of the other half-cell. A brass disk *A* with machined annular and radial slots was screwed into a circular recess in the center of each wall with its grooved surface countersunk 2×10^{-3} cm. below the cell face. The two disks were platinum plated and served both as membrane supports and electrodes. A binding post *H* connected to each electrode served as an external contact. The glass reservoir *E* for permeant supply and an open calibrated horizontal capillary *G* for observing the rate of flow were attached to the holes *C* by means of standard taper joints. The channel *D* in each half-cell was sealed with a screwed tapered plug and was used for filling and venting.

The cells were placed in an air thermostat maintained at $30.0 \pm 0.1^\circ \text{C}$.

In carrying out a permeability measurement, the membrane was first accommodated to the permeant by transferring it from the acetone and immersing it in the permeant for at least two hours. The thickness of the immersed membrane was measured with a micrometer caliper. Several readings were taken with a mean deviation of about 5%. The rate of flow of the permeant through the membrane under a given pressure gradient was observed in the capillary *G* (Fig. 1) over a period of about two hours. The pressure was applied by means of air in the reservoir *E* and was measured on a differential xylene manometer. A series of such flow rates at different pressure gradients, both positive and negative, was determined.

A plot of flow rate versus pressure gradient always yielded a straight line. The slope of this line provided an average value of the flow rate under unit pressure gradient without any need of a correction for capillarity in the flow tube *G*. A deviation from linearity indicated a leak in the system and such results were discarded.

In calculating the permeability coefficient *K*, it was assumed that the area of membrane accessible to flow was the "free area", i.e., the total area of membrane in the cell less that of the ridges of the supporting plates *D*, which were impressed on the membrane surface. It was established experimentally that this assumption led to absolute permeability coefficients which were as much as 10% too low.

Conductances were measured on a Jones Conductance Bridge, using an external shunt on one ratio arm to provide a ratio of 1 to 11. This was found necessary to give adequate sensitivity at the low values of resistance found.

A standard conductance cell was used as an auxiliary in order to measure the conductance of the solution before and after contact with cellophane. These duplicate measurements were made to ensure that no further adsorption on the membrane had occurred during a permeability measurement. No change in conductivity was noted when using membranes that had been stored more than 12 hr. in the permeant. On completion of each permeability-conductance experiment the cell was opened, the membrane removed, and the cell reassembled without any membrane. It was then refilled with the same solution and the resistance again measured. The resistance of the membrane was taken to be the difference of the two measured resistances.

Determination of Imbibition

Several methods were tried, all based on the principle of weighing the liquid imbibed in the membrane. The method finally adopted consisted in measuring the rate of drying of the membrane. It was found that the drying curve consisted of two straight lines of different slope corresponding to two different rates of drying. The point of intersection was assumed to correspond to the point of transition between evaporation of liquid from the surface and from the interior of the membrane.

A piece of cellophane, accommodated to the permeant, cut square so that its area could be determined readily, was blotted free of the bulk of the liquid adhering to the surface and suspended vertically on the weighing arm of a chainomatic balance. Its weight was taken every 30 sec. for about 20 min. A typical curve is shown in Fig. 2. After this weighing, the cellophane was

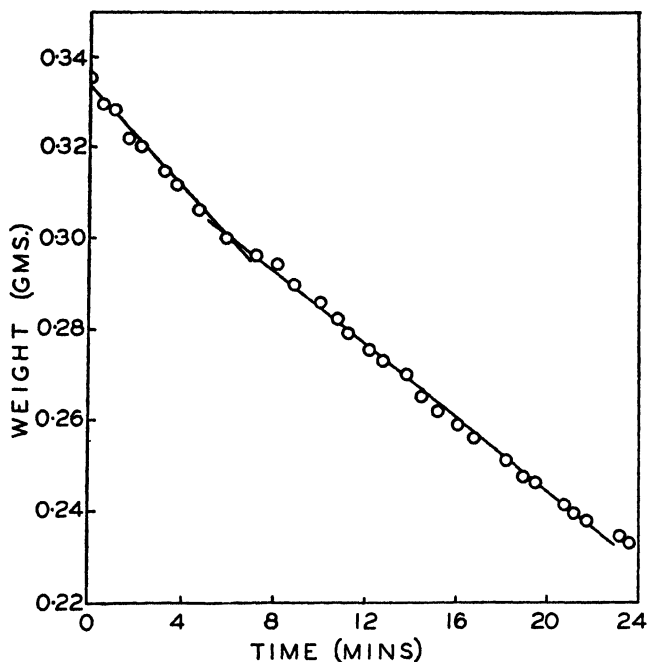


FIG. 2. *Drying curve of a water soaked membrane.*

dried in an oven at 130°C . for a period of two hours, and its dry weight determined. The difference between the interpolated value of the wet cellophane and the dry weight was taken to be the weight of the imbibed liquid. The pore volume per unit area was obtained by dividing this weight by the area of the cellophane and the density of the liquid. With aqueous solutions, the weight of residual solute was negligible.

The drying rate method was found to give more reliable and consistent results than the conventional method of blotting the soaked membrane free of excess liquid and weighing (5).

Results

Effect of Viscosity

In order to check the validity of Equation (1), the permeability P of water through the swollen membrane was measured at various temperatures. The results, given in Table II, indicate that at a fixed degree of swelling P varies inversely with the viscosity of the permeant. This together with the fact that in all cases the rate of flow Q was found proportional to the pressure gradient is taken as fairly conclusive evidence of a viscous type of flow.

TABLE II

EFFECT OF VISCOSITY ON THE PERMEABILITY OF A WATER SWOLLEN MEMBRANE

$T, ^\circ\text{C.}$	$P, \text{gm.}^{-1} \text{cm.}^2 \text{sec.} \times 10^{11}$	$\eta \text{ (poises)} \times P \times 10^{13}$
20	1.95	1.95
25	2.17	1.93
28	2.28	1.91
33.5	2.65	1.97
38	3.08	2.02
40	3.30	2.07

Effect of Swelling on Permeability

A large number of determinations of the permeability of various liquids was made at various degrees of swelling. Table III includes the data obtained

TABLE III

EFFECT OF SWELLING ON PERMEABILITY COEFFICIENT

Permeant	Membrane treatment	$L, \text{cm.} \times 10^3$	$K, \text{cm.}^2 \times 10^{16}$
Water	Water	8.0	15.8
3%NaOH	3% NaOH	9.5	21.3
6% NaOH	6% NaOH	10.5	25.6
Methanol	60% Ethanol	4.5	0.94
	Water	7.7	3.57
	3% NaOH	9.5	5.22
Ethanol	60% Ethanol	4.5	7.52
	Water	7.7	2.58
	3% NaOH	10.0	4.17
Acetone	60% Ethanol	4.5	0.87
	Water	8.0	3.07
	3% NaOH	9.0	5.00

using methanol, ethanol, acetone, water, and sodium hydroxide solutions as permeants. It will be noted from this table and a plot of K versus membrane thickness (Fig. 3) that an approximately fourfold increase in the permeability coefficient of the organic permeants resulted from increasing the thickness from 4.5×10^{-3} cm. by swelling in water. Additional swelling by treatment of the membrane with sodium hydroxide caused a further increase in permeability. Similar results obtained with a variety of alcohols, ketones, and miscellaneous organic liquids are shown in Table IV.

The most striking feature of these results is that the permeability coefficients corresponding to a given membrane thickness fall into two clearly distinct classes, one for organic and the other for aqueous permeants. Thus

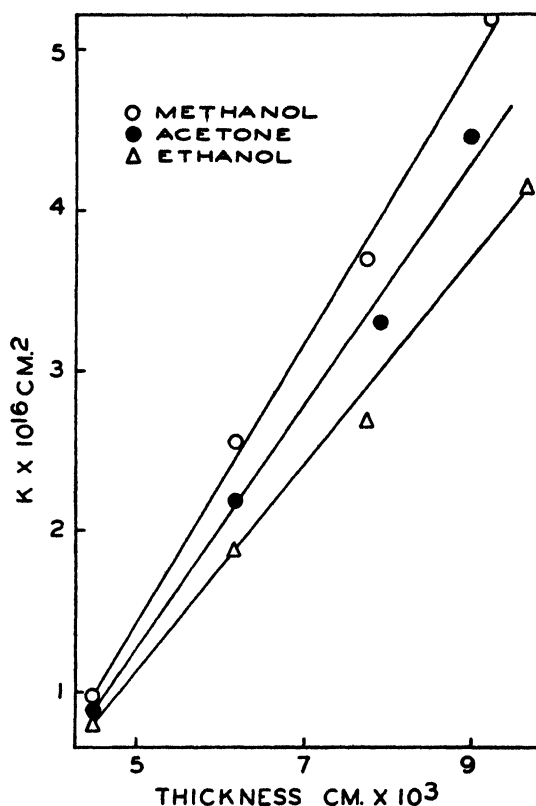


FIG. 3. Variation of permeability coefficient with thickness of swollen membranes.

for water swollen membranes having approximately the same thickness, K of organic liquids was about one-fifth that of water.

Permeability to Homologous Series

Permeability determinations were made with homologous series of liquids on treated membranes to observe the effect of lengthening of the carbon chain. The series included alcohols and ketones. A number of miscellaneous liquids were also examined, including chloroform and carbon tetrachloride because of their frequent use in osmometry.

Values of the thickness, permeability, and permeability coefficients are given in Table IV. In addition to the effect of swelling in increasing P and K , attention is drawn to the following points.

(1) Corresponding to a given membrane treatment, the resulting membrane thickness is approximately the same for all permeants except in the case of the ketones, where a decrease in thickness with increasing chain length is shown.

TABLE IV
PERMEABILITY OF ORGANIC LIQUIDS

Permeant	60% Ethanol			Water			3% NaOH		
	$L, \text{ cm.} \times 10^3$	$P, \text{ gm.}^{-1}\text{cm.}^3 \text{ sec.} \times 10^{11}$	$K, \text{ cm.}^3 \times 10^{16}$	$L, \text{ cm.} \times 10^3$	$P, \text{ gm.}^{-1}\text{cm.}^3 \text{ sec.} \times 10^{11}$	$K, \text{ cm.}^3 \times 10^{16}$	$L, \text{ cm.} \times 10^3$	$P, \text{ gm.}^{-1}\text{cm.}^3 \text{ sec.} \times 10^{11}$	$K, \text{ cm.}^3 \times 10^{16}$
Alcohols									
Methanol	4.5	0.41	0.94	7.7	0.92	3.6	9.5	1.1	5.2
Ethanol	4.5	0.17	0.75	7.7	0.35	2.6	10.0	0.33	4.2
Propanol	4.5	0.083	0.64	7.7	0.16	2.1	9.5	0.21	3.4
Butanol	4.5	0.061	0.61	7.7	0.11	1.8	9.0	0.12	2.6
Ketones									
Acetone	4.5	0.60	0.87	8.0	1.30	3.1	9.0	1.9	5.0
Butanone-2	4.5	0.44	0.72	8.0	0.96	2.8	8.8	1.4	4.7
Pentanone-2	4.5	0.29	0.63	7.5	0.78	2.7	8.5	1.1	4.4
Hexanone-2	4.5	0.24	0.58	7.0	0.68	2.5	8.0	1.0	4.2
Heptanone-4	4.5	0.16	0.51	6.2	0.55	2.4	7.5	0.74	3.9
Octanone-2	4.5	0.13	0.45	6.0	0.45	2.0	7.5	1.0	3.6
Miscellaneous									
Ethyl acetate	4.5	0.38	0.69	7.5	0.50	1.4	8.5	0.53	1.8
Methyl propionate	—	—	—	7.6	0.48	2.2	8.0	0.54	1.8
Ethyl propionate	—	—	—	7.6	0.42	1.3	8.0	0.47	1.7
Chloroform	4.5	0.27	0.62	7.5	0.34	1.3	8.0	0.31	1.4
Carbon tetrachloride	4.5	0.13	0.52	7.5	0.17	1.1	8.0	0.19	1.2
Benzene	—	—	—	7.5	0.26	1.1	8.0	0.26	1.2
Toluene	—	—	—	7.6	0.24	1.0	8.0	0.24	1.0
Nitrobenzene	—	—	—	7.6	0.09	1.2	—	—	—
Hexane	—	—	—	7.6	0.36	0.85	8.0	0.40	1.0
Heptane	—	—	—	7.6	0.26	0.76	8.0	0.30	0.88

(2) For a given membrane treatment, the permeability coefficients of the homologous series of alcohols and ketones decrease progressively with increasing number of carbon atoms. The effect is shown for the ketones in Fig. 4.

(3) The permeability coefficients of the liquids that are insoluble in water, mainly in the miscellaneous group, are consistently lower than those of the water soluble liquids. The data on this group also show that water and caustic treatments cause relatively small increases in K .

(4) There is little difference in K for benzene and nitrobenzene. Since Martin and Gortner (12) report that in the presence of benzene and nitrobenzene, the respective zeta potentials of cellulose are zero and -142 mv., this indicates the absence of appreciable electroviscous effects.

Void Volume and Capillary Structure

In order to compute the effective pore radius and pore number by means of Equations (4) and (5) it was necessary to know the void fraction ϵ . This was computed by dividing the volume of liquid imbibed per unit area (as

determined by the weighing method) by the measured membrane thickness. This procedure assumes that all the imbibed liquid is contained in pores and is available for liquid flow.

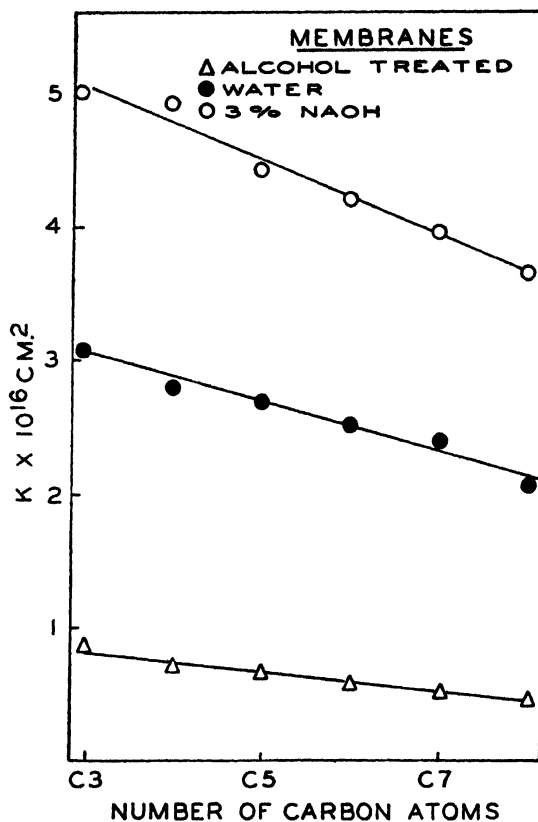


FIG. 4. Variation of the permeability coefficient of ketones with number of carbon atoms for different membrane treatments.

Since the volumes of a mixture of cellulose and a liquid that does not react chemically with the cellulose are additive (6), ϵ can be calculated from the relation

$$\epsilon = 1 - \frac{0.62 W}{L},$$

where 0.62 is the specific volume of cellulose and W is the weight of cellulose in grams per square centimeter of swollen membrane. This should apply to all the permeants listed in Tables III and IV with the possible exception of the sodium hydroxide solutions.

Values of ϵ obtained by the two methods are given in Table V. Good agreement is shown only with water and 3% sodium hydroxide. The two methods give self-consistent results with 6% sodium hydroxide, but there is a significant difference between the two sets. In the case of the alcohols, there is wide divergence. Values of ϵ calculated from the void

TABLE V
COMPARISON OF VALUES OF VOID FRACTION

Permeant	Membrane treatment	ϵ	
		From void volume	From thickness
Water	Water	0.64	0.62
		0.62	0.615
3% NaOH	3% NaOH	0.54	0.54
6% NaOH	6% NaOH	0.55	0.66
	6% NaOH	0.56	0.66
	6% NaOH	0.54	0.67
Methanol	60% Ethanol	0.18	0.38
	Water	0.17	0.59
	3% NaOH	0.17	0.62
Ethanol	60% Ethanol	0.21	0.38
	Water	0.12	0.59
	3% NaOH	0.10	0.62
Propanol	60% Ethanol	0.32	0.38
	Water	0.18	0.56
	3% NaOH	0.16	0.63
Butanol	60% Ethanol	0.27	0.37
	Water	0.20	0.59
	3% NaOH	0.14	0.62

volume are much lower than those computed from the thickness. Similar differences were shown for the remaining permeants listed in Table IV.

The discrepancy between the values obtained by the two methods for the organic permeants reveals an error in one or both methods. The simplest explanation, which is discussed later, is that effective thickness is incorrectly measured as the result of a structural contraction which is not detected by the micrometer caliper. If such is the case both values are in error since the thickness measurement is used in computing both quantities. This will have the further effect of yielding values of K , which, for purposes of calculating capillary dimensions, are spurious, since the permeability coefficient is computed from the measured P and the membrane thickness.

If Equations (4) and (5) are applicable, we are justified only in using the K and ϵ values for water and 1% sodium hydroxide and 3% sodium hydroxide to compute the effective pore radius and the pore number. These values are shown in Table VI and include the data for 6% sodium hydroxide, ϵ being taken to be 0.55. The value of r computed for the water in water swollen membrane thus obtained compares favorably with values of 2 to 3×10^{-7} cm. calculated by McBain and Kistler (8) from the pressure required to blow air through a water soaked cellophane and 1.3×10^{-7} cm. estimated by

TABLE VI
AVERAGE PORE RADIUS AND PORE NUMBER

Permeant	Treatment of membrane	Average pore radius, cm. $\times 10^7$	Pore number $\times 10^{-12}/\text{cm.}^2$
Water	Water	1.4	9.1
3% NaOH	3% NaOH	1.7	5.6
6% NaOH	6% NaOH	2.0	2.2

Manegold and Viets (11) using the permeability - void volume method. It is interesting to note that these values of the pore radii are similar to those of collodion membranes of void fraction *circa* 0.60 (5).

Permeability-conductance Measurements

The results of a series of permeability conductance measurements on water swollen membranes, using potassium chloride solutions ranging from 0.002 *M* to 0.1 *M*, are given in Table VII. It will be noted that the *P* values are

TABLE VII
PERMEABILITY-CONDUCTANCE DATA FOR WATER SWOLLEN CELLOPHANE

Molarity KCl	<i>P</i> , gm. ⁻¹ cm. ² sec. $\times 10^{11}$	<i>C</i> , mhos cm. ⁻² $\times 10^2$	κ/C , cm. $\times 10^2$
0.002	2.38	1.12	2.60
0.005	2.26	2.01	3.53
0.008	2.46	2.61	4.35
0.010	2.21	3.08	4.60
0.020	2.15	5.05	5.39
0.040	2.46	8.53	6.37
0.060	2.58	11.92	6.64
0.080	2.52	15.25	6.79
0.100	2.14	18.73	6.92

reasonably constant. Values of κ/C on the other hand increase progressively with increasing concentration as the result of surface conductance, which tends to give high values for *C*. These results are similar to those obtained by Manegold and Solf (10) for potassium chloride solutions in collodion membranes of pore radii ranging from 6.5×10^{-7} to 20×10^{-7} cm., except that κ/C reached a constant value above 0.03 *M*.

To eliminate the error due to surface conductance, values of κ/C are plotted against (concentration)⁻¹ and extrapolated to infinite concentration, at which point surface conductance is believed to become negligible (Fig. 5). This yields a κ/C value of 7.5×10^{-2} cm. The value of *r* calculated from these data using Equation (7) is 3.4×10^{-7} cm. This is 2.5 times as great as that computed from the permeability - void fraction data of water in water swollen

cellophane. This agreement however is illusory, as can be seen by computing the effective void fraction from the conductivity and thickness. A comparison of Equations (3) and (6) shows that $\epsilon = \frac{LC}{\kappa}$, from which ϵ is calculated to be 0.11, i.e., about 1/6 the value given in Table V for water. Manegold and

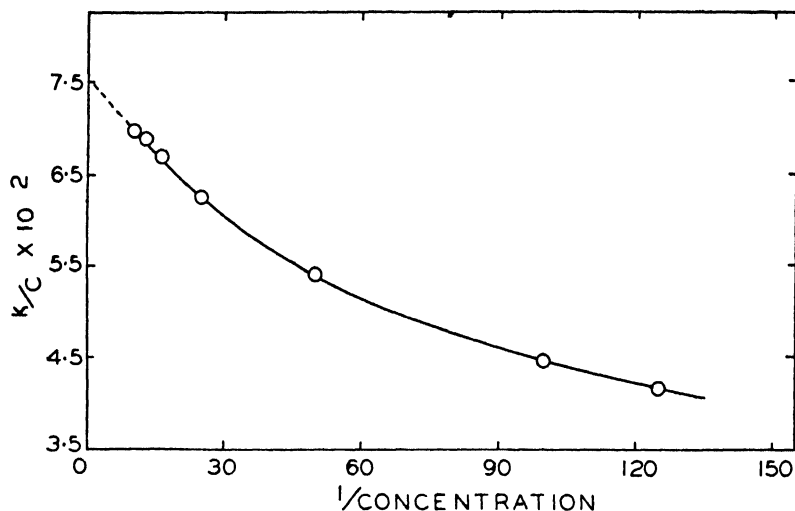


FIG. 5. Extrapolation of κ/C to eliminate surface conductance effect.

Solf (10), in the measurements on collodion membranes referred to above, found that this ratio had a value of from 1/3 at low pore sizes increasing with increasing pore sizes to 2/3, and they attributed the effect to an irregular slit structure, together with possible closed pores.

If instead of the simple cylindrical capillary network, a more general structure is assumed with pores of any shape and various orientations θ to the normal of the sheet and that Ohm's law applies, it is readily shown that Equation (6) assumes the form:—

$$\frac{LC}{\kappa} = \overline{\cos^2 \theta} \cdot \epsilon.$$

Thus if the entire imbibed volume is operative in electrical conduction, as it is assumed to be in liquid permeation, $\overline{\cos^2 \theta} = 1/6$ for the water swollen cellophane. For orientation normal to the sheet $\overline{\cos^2 \theta} = 1$ and for random orientation $\overline{\cos^2 \theta} = 1/2$. Hence if the conductivity method is valid the results indicate the existence of either closed pores or marked pore orientation in the plane of the sheet. The results, while not conclusive, therefore cast doubt on the validity of using the measured void volume in Equation (2).

Discussion

It is evident from these results that the rate of flow of liquids through cellophane is not defined by a permeability coefficient which depends solely on the thickness of the swollen sheet.

It has been demonstrated for the case of water that viscous type flow occurs, i.e., the rate of flow varies directly with the pressure gradient and inversely with the viscosity. The method of liquid replacement followed in accommodating swollen membranes to the various permeants produces little change in the thickness of the membrane and hence presumably in the degree of swelling. This agrees with current views on the phenomena of swelling in cellulose (15).

An increase in thickness results in an increased K , although the increase depends upon the nature of the permeant. This is of considerable practical importance in preparing cellophane membranes in osmometry, as has been pointed out by McIntosh *et al.* (14). The relatively small increase in the case of water-insoluble permeants is of interest and may be partly attributed to incomplete removal of the water. The small variation in K of various organic liquids can be attributed jointly to small variations in the degree of swelling as measured by the thickness and to steric effects.

The large differences in permeability between aqueous and organic permeants through membranes of the same thickness is however entirely inconsistent with the Bechhold (1) type of capillary structure, unless the additional assumption is made that internal changes in the capillary network occur that do not reveal themselves by changes in external dimensions.

The measured values of the void fraction show a similar anomaly. Only in the case of water and 1% sodium hydroxide solutions do the values calculated from the imbibition-thickness and the thickness alone agree. With the organic permeants there is a large discrepancy between the two sets of values. Moreover, the volumes of organic liquids imbibed are less than half those of aqueous solutions at the same membrane thickness.

The only explanation that we can offer at the present time is that, on replacing the water by any of the organic permeants listed in Table IV, a reduction in the degree of swelling occurs that is not detected in measuring the thickness. This may be envisaged as a microscopic or submicroscopic wrinkling of the surface that does not materially change the distance separating the "high spots" in the structure. Since cellophane is precipitated in an aqueous medium, i.e., the sheet is formed in the water swollen state, this hypothesis explains why agreement in the void fraction values is obtained with water. It also explains the anomalies between the permeabilities and void fractions of water and organic liquids.

The difference in the results of the permeability-void volume and permeability-conductance methods is difficult to account for except by imposing further qualifications of the capillary network structure.

Thus, while the results presented here can be explained by a mechanism of viscous flow through a capillary network whose internal dimensions are determined jointly by the thickness and the permeant, the evidence in favor

of such a mechanism is inconclusive. It is our belief however that permeability measurements provide a useful method of studying the phenomenon of swelling of cellulose, and are being studied further.

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THE ELASTIC PROPERTIES OF SILICA GELS

By L. A. MUNRO, J. G. McNAB, AND W. L. OTT

Abstract

The effect of age, concentration, and temperature on the Young's modulus of acid and alkaline silica gels has been measured by a compression method. For the range of concentrations used the Young's modulus is not independent of load. The modulus increases with age of the gel and with concentration. Hurd's criterion of the time of set (tilted rod method) has been evaluated in terms of absolute units. The effect of temperature on the elastic properties is different for acid and alkaline gels. The Young's modulus values for the former (pH 5.6) increase, while for the alkaline gel (pH 8.2) of the same silicate concentration the values decrease with increasing temperature. The modulus for the alkaline gel is higher than for the acid gel at the lower temperatures. A mechanism is suggested to explain these differences.

Introduction

In the setting of a gel, viscosity changes take place with time, until the sol becomes semirigid. The time of set has been defined in a number of ways, e.g., the time at which the gelling mixture will no longer flow from an inverted test tube. More consistent values are obtained by the method proposed by Hurd and Letteron (6). This measures the time for a gel to reach a rigidity that will support a glass rod 10 cm. by 3 mm. when inserted at an angle of 20° from the vertical. According to Prasad, Mehta, and Desai (13) the time of set is the time at which the extinction coefficient reaches a maximum. The latter method is of limited value with opaque, rapid-setting, alkaline gels. Other methods were used by Flemming (3) and by Batchelor (1).

It is certain that the gelation process continues beyond the time of set determined by any of the above methods. This is indicated by an increase in the rigidity with time, by syneresis, and by other phenomena.

The elastic properties of silica gel and of other inorganic gels have been recognized qualitatively for some time. However, there are in the literature very few systematic quantitative data on the elastic properties. Kröger and Fischer (9) studied the bending of rods of silica gels of one concentration of silica only (Na_2SiO_3 solution, 15% SiO_2) but containing different concentrations of acid. They reported that the elastic properties, i.e., Young's modulus, decreased continuously with a change from acid to alkaline gels. Hatschek (4) in a study of the elastic properties of several kinds of gels (agar, gelatin, and silica) determined the Young's modulus of one sample of a silica gel made by mixing 35 ml. of sodium silicate (sp. gr. 1.15) with 30 ml. of

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ont.

6 *N* hydrochloric acid. The pH of the gel was unstated. Using a compression method, he found that for this concentrated gel the modulus was independent of the load used and that the modulus increased with age. Hatschek concluded that, "further study of the elastic properties of gels over a large range of conditions should afford a deeper insight into their structure."

The present work was undertaken to extend the meager data at present available. The modulus of silica gels differing in concentration, pH, and age have accordingly been measured over a range of temperature by a compression method, using different loads. Hurd's criterion of "setting" has been evaluated in absolute units.

Experimental

The apparatus for the modulus determination is illustrated in Fig. 1. It consists of a vertical plunger with plates 4 cm. in diameter supported by a brass base 15 cm. in diameter equipped with three leveling screws. The movement of the plunger is kept vertical by two cross bars. This apparatus has the advantage over that used by Hatschek (4) in that the friction and the initial load due to the plunger are less. The weight of the aluminum plunger is 27.0 gm. Successive loads are applied by the addition of weights to the top plate. These weights were made by pouring slightly more than 25 gm. of molten Wood's metal into beakers and then filing the resulting disk to an accuracy of 0.01 gm.

For gels with times of set greater than five minutes, the samples were prepared by mixing suitable concentrations of sodium silicate and acetic acid solutions according to the method previously described (10). The pH was determined colorimetrically, since the glass electrode deteriorates in the presence of the silicate. The time of set was determined on separate samples by the method of Hurd and Letteron (6). For the test pieces 10 ml. aliquots were pipetted into standard vaseline-coated brass cylinders resting on a vaselined glass plate in a thermostat. For the higher temperature the glass plate was coated with a thin layer of high melting paraffin onto which the vaselined cylinder was placed immediately. Initially, the setting mixture was then covered with a thin layer of light paraffin oil to prevent evaporation. In our later experiments the oil was not added until immediately before setting. This gave a flatter surface.

For rapid-setting gels (times of set less than five minutes) 5 ml. of the sodium silicate solution was stirred vigorously into 5 ml. of acetic acid solution in the cylinders. The silicate was always added to the acid, to avoid localized gelation. Although with such a method the preparation of duplicate specimens free from inherent strains is obviously difficult, the agreement shown by the data has justified the procedure.

The above procedures gave test pieces 2.55 ± 0.05 cm. in diameter and 1.9 ± 0.15 cm. in length, with ends having almost plane surfaces. The specimens were aged in a thermostat for the desired time and then transferred to a small glass plate and placed in the instrument enclosed in a glass air

PLATE I

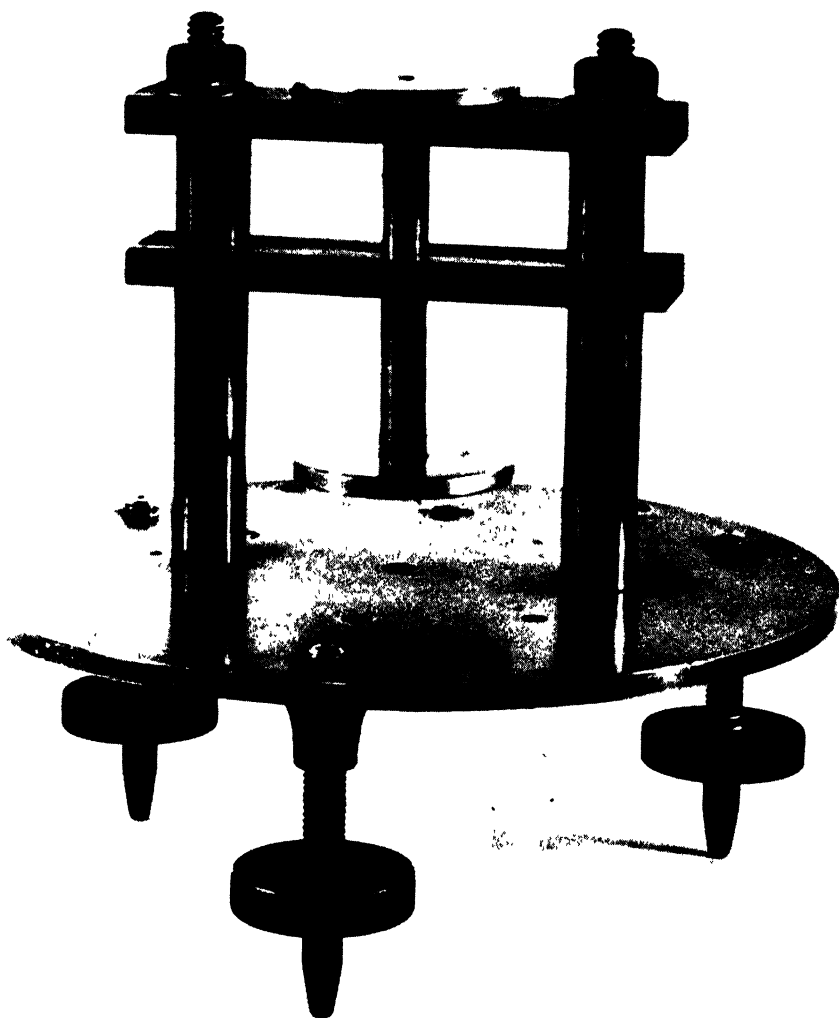


FIG. 1. *Apparatus.*

thermostat at 90 to 100% relative humidity. The dimensions of the test piece were measured by means of cathetometers. Changes in dimensions under load were measured to 0.05 mm. All readings were made 15 sec. after the load was applied.

The Young's modulus (grams per square centimeter) = $\frac{WH(1 + \Delta H)}{\pi r^2 \cdot \Delta H}$,
 where W = Load in grams,
 H = Height in centimeters,
 ΔH = Change in height,
 r = Radius of specimen.

Corrections were made for the change in cross-sectional area due to compression (5) for each load. These amount to a maximum of $\pm 6.2\%$ of the modulus values.

For duplicate gels prepared in sequence the modulus values agree within 1 or 2%. The data for gels prepared some years apart using different silicate showed a maximum deviation of 11%. Typical data for two such gels are given in Table I.

TABLE I
REPRODUCIBILITY OF YOUNG'S MODULUS (E)

pH, 5.6
 Temp., 20° C.
 Load, 77 gm./15 sec. readings
 Silicate conc., 4.4% SiO₂
 Time of set, 83 min.
 Gel 1—(prepared and tested 1932, J.G.M.)
 Gel 2—(prepared and tested 1948, W.L.O.)

Age, hr.	Gel 1 E_1 , gm./cm. ²	Gel 2 E_2 , gm./cm. ²	Diff. $\frac{E_1 - E_2}{E_1}$, %
10	126.5	125.0	+ 1%
24	136.6	143.0	- 5%
52	153.0	153.0	0%
75	155.8	155.0	+ 0.5%
100	182.2	162.0	+11%

The Effect of Load

Hatschek reported that the modulus of the concentrated gel used in his experiments (12%) was independent of load. Unfortunately with such a high concentration a study of the relation of modulus to the time of set is impossible except at very low or very high pH values. In the present work duplicate results were obtained only when the same loads were used, as is indicated in Table II, which gives the data for a typical case. In the experiments on the effect of concentration, age, and temperature the data for a load of 77 gm. was used throughout except for the comparison of the modulus of acid gels differing in concentration. In the latter case (Figs. 2 and 3) a load of 52 gm. was used because of the fragility of the 3.3% gel. In general the determined value of Young's modulus decreases with increasing load.

TABLE II

VARIATION OF YOUNG'S MODULUS WITH DIFFERENT LOADS (E)

pH, 3.6

Silicate conc., 6.6% SiO_2

Temp., 20° C.

Time of set, 364 min.

Specimen	Age, hr.	E , gm./cm. ² Load = 227 gm.	E , gm./cm. ² Load = 127 gm.
1	18	233.0	273.0
2	42	330.0	376.0
3	66	376.0	388.0
4	90	379.0	390.0
5	114	418.0	449.0
6	138	420.0	483.0

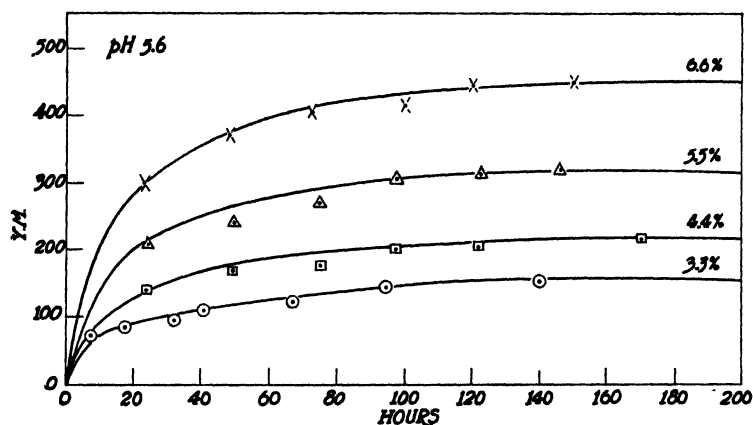


FIG. 2. Change of Young's modulus with age for silica gels of pH 5.6 and different concentrations under 52 gm. load.

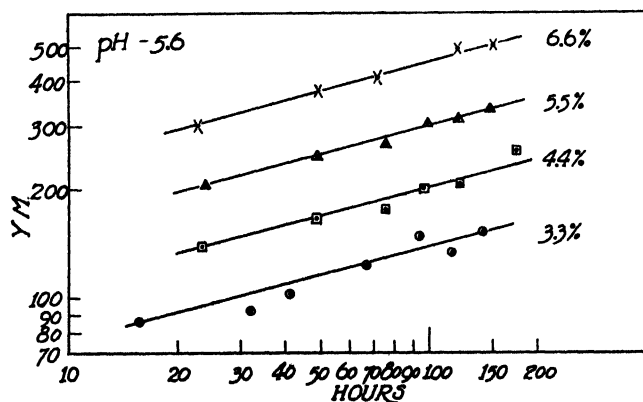


FIG. 3. Logarithmic curves showing the change in Young's modulus with age of gels of pH 5.6 and different silica concentrations under 52 gm. load.

The Effect of Age

Since the gelation process continues beyond the time of set, it is to be expected that the Young's modulus will increase until a constant or maximum value is reached. Fig. 2 shows the change in modulus with time, for gels of

pH 5.6, using a 52 gm. load. The numerical data for these and subsequent curves have been omitted in order to save space.

The Effect of Concentration

The dependence of modulus values on the concentration is indicated in Figs. 3 and 4 for gels of pH 5.6 and 8.2 to 8.9 respectively. In Fig. 5 the

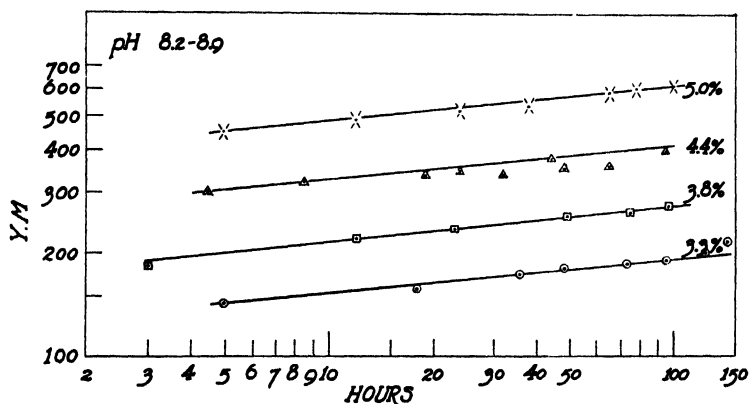
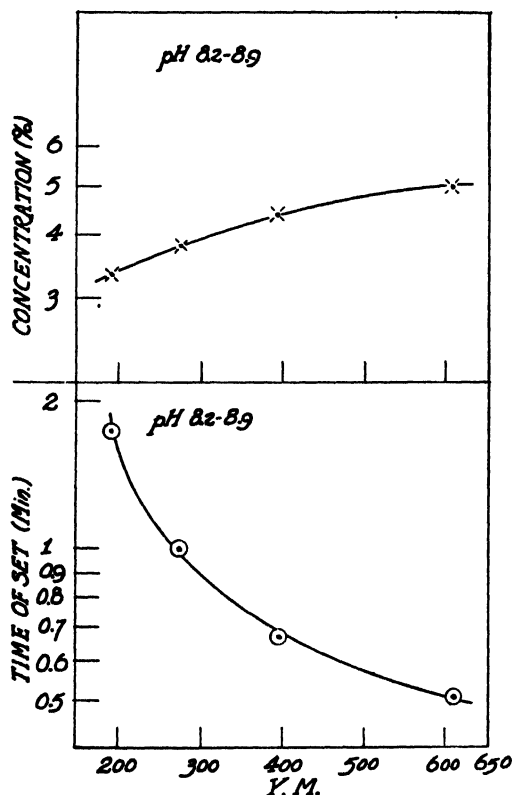


FIG. 4. Logarithmic curves showing the change in Young's modulus with age of gels of pH 8.2 and different silica concentrations under 77 gm. load.



FIGS. 5 AND 6. FIG. 5 (top). Change of Young's modulus with silicate concentration of gels of pH 8.2 to 8.9, using 77 gm. load. FIG. 6. (bottom). The relation between the Young's modulus and time of set, using 77 gm. load.

modulus values for 100-hr. gels are plotted against concentration and in Fig. 6 are contrasted with the times of set. The same type of curve is obtained with the 24-hr. values for the modulus. The rapid-setting gels develop the highest final modulus values.

The Effect of Temperature

The effect of temperature on the gelation process for gels of pH 5.6 and 8.2 to 8.9 is illustrated by Figs. 7 and 8. Both sets of gels were prepared from the 4.4% SiO_2 silicate.

The Relation between the Modulus and Time of Set

The tilted rod method of determining time of set used by Hurd and his coworkers is of course a measurement of the time required for the gel system to reach an arbitrary degree of rigidity, i.e., a certain modulus. Initially Hurd and Letteron (6) used a Pyrex rod 8 cm. long and 3 mm. thick. This was inserted into the gelling mixture at an angle of 20 degrees from the vertical and the time was taken when the gel had sufficient rigidity to support it. In later work (7) a 10 cm. rod was used; this would require higher modulus values as the criterion of set. Values will be constant only if the depth of gel is constant, so that beakers of the same dimensions should be used.

In an attempt to evaluate Hurd's useful criterion of the setting time of a gel in terms of absolute units, the curves for Young's modulus values versus time are extrapolated to the time corresponding to the original time of set of the gel at the given temperature. It is apparent from Figs. 7 and 8 that this procedure gives a constant modulus. For the alkaline gels (Fig. 8) the value is 156 gm. per cm^2 . The data from which Fig. 7 was constructed were obtained several years afterwards. The values are constant but somewhat lower (122 gm. per cm^2). This is undoubtedly due to the factors mentioned above. The agreement between values determined under the same experimental conditions and apparatus is surprisingly good.

Discussion

When the log time of set is plotted against the pH of the silica gel, the curve goes through a sharp minimum (11). It has been shown that the mechanism of the setting process is different for gels on opposite sides of the minimum set (12). This was indicated by the marked change in the slope of the curves log time of set vs. $1/T^\circ\text{A}$, and by the contrast in the effect of addition agents (10). Further, syneresis, which is the exudation of dispersion medium accompanied by shrinkage of the gel, takes place rapidly with alkaline gels and slowly with acid gels of the same concentration.

In the present work one gel is on the acid side and the other is close to the pH of minimum time of set for gels of this concentration (11). In both cases the plot of the time of set vs. the reciprocal of the absolute temperature gives

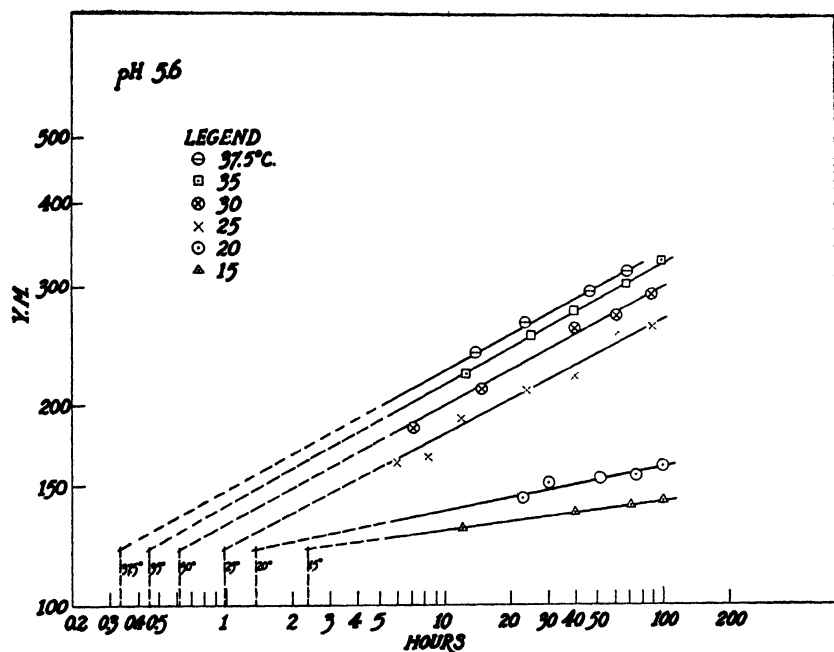


FIG. 7. Young's modulus for gels from 4.4% SiO_2 silicate at different temperatures plotted against age and extrapolated to times corresponding to the times of set. pH 5.6. Load, 77 gm.

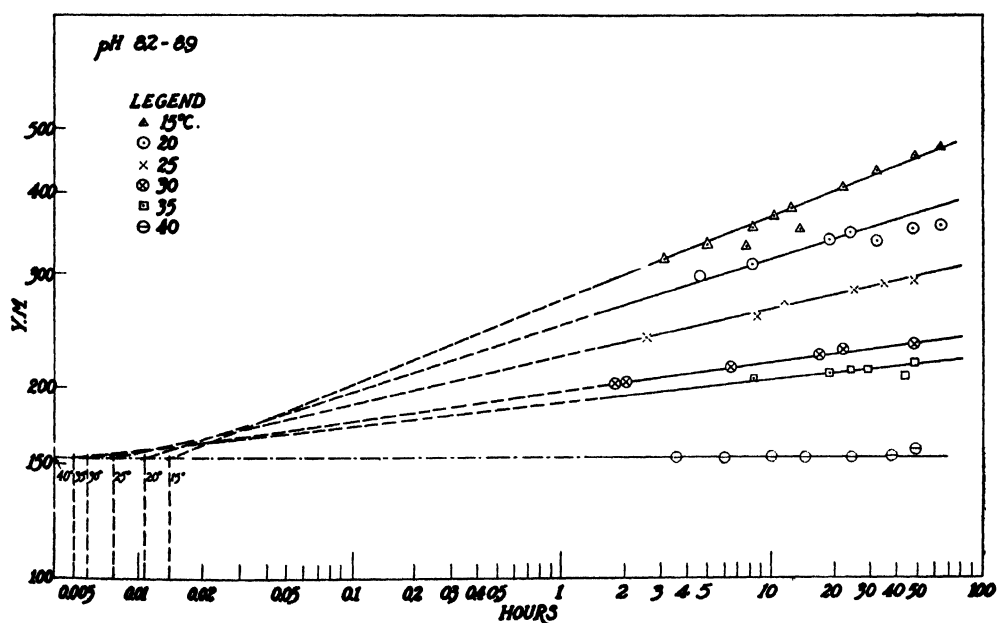


FIG. 8. Young's modulus for gels from 4.4% SiO_2 silicate at different temperatures plotted against age and extrapolated to times corresponding to the times of set. pH 8.2 to 8.9. Load, 77 gm.

straight lines (Figs. 9 and 10). Fig. 11 gives the modulus values at 100 hr. plotted against $1/T^\circ\text{A}$. The curve for the acid gel shows an increase with increasing temperature while the curve for the alkaline gel shows a decrease.

An unexpected observation is that the Young's modulus of the alkaline gel at room temperature is higher than that of the acid gel of the same silicate concentration. The recovery of the alkaline gel on removal of the applied

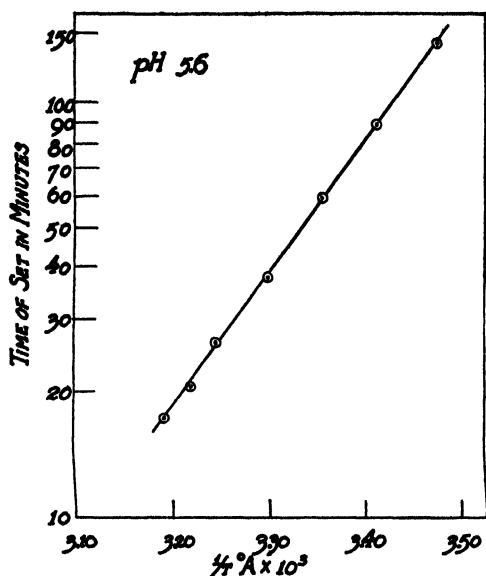


FIG. 9. Variation of time of set with the reciprocal of the absolute temperature for silica gels of pH 5.6 from 4.4% SiO_2 silicate.

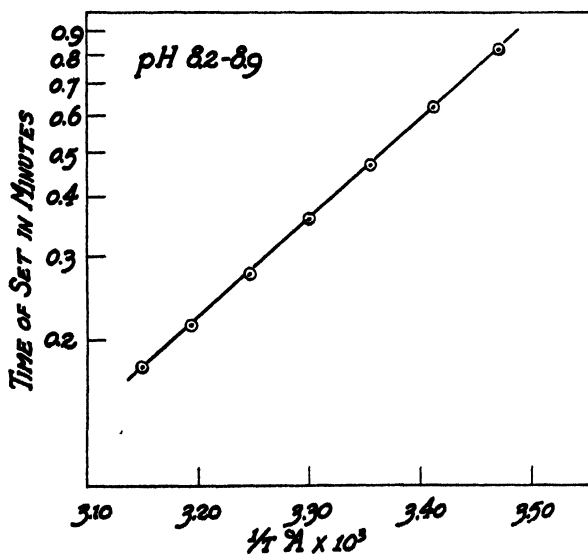


FIG. 10. Variation of time of set with reciprocal of the absolute temperature for silica gels of pH 8.2 from 4.4% SiO_2 silicate.

load is less than that for the acid gel, i.e., the elasticity is less. The above facts and the difference in the effect of temperature on the modulus of acid and alkaline gels must be explained by any suggested mechanism.

It has been shown (8, 12) that for gels of pH greater than 8.5 (approximately) the plot of log time of set vs. $1/T^\circ\text{A}$ deviates from a straight line; this indicates a second effect in the gelation process.

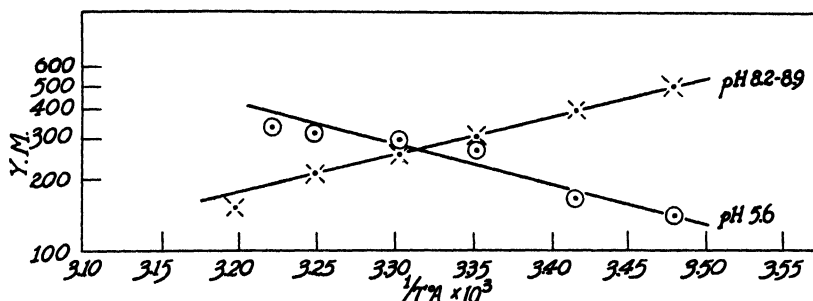


FIG. 11. The 100 hr. Young's modulus values for an acid and an alkaline gel plotted against the reciprocal of the absolute temperatures. Silicate, 4.4% SiO_2 . Load, 77 gm.

Carman (2) has suggested that in alkali media there is a strong tendency toward the destruction of the Si-O-Si links, with the production of smaller aggregates. Hurd (8) considers that "strong alkali reverses the process which occurs during gelation". He believes that "alkaline gels are softer and less elastic than acid gels since condensation and cross linkage formation probably do not proceed so far in alkaline gels."

While the straight line in Fig. 10 would suggest that the degradation of the polymer or peptizing effect of the alkali is not as pronounced as at higher pH values, nevertheless Fig. 11, which shows that the modulus of the 8.2 gel decreases with increasing temperature, would indicate that this effect is present.

The increase in modulus with temperature for the acid gels (Fig. 11) can be explained by the production of additional linkages by further condensations at the higher temperatures. This is in agreement with the observation of Schwarz and Stöwener (14) that acid silica gels prepared at 100°C . adsorbed less methylene blue than a gel prepared at 0°C ., which observation is interpreted as meaning that the total surface of the high temperature gel is less than that of the low temperature gel. If the increase in modulus were due to a larger number of smaller particles, as is obtained in linear polymerization at higher temperatures, the adsorption would be *greater*, not less.

It is well known that freshly precipitated silica gel may sometimes be peptized by acid or alkali while an aged gel cannot. This also indicates that the observed increase in Young's modulus with age is not associated with an increase in total surface such as would be obtained if additional small polymers were formed. It rather points to cross linkages, as suggested above. Indeed, it has long been observed that in many instances sols increase in particle size by forming chainlike or branched structures. The modulus of all gels increased with age.

The fact that the modulus of the alkaline gel at the lower temperature is *higher* than that of the acid gels of the same concentration may indicate that in

the alkaline medium gelation produces the Von Weimarn (BaSO_4) type of gel with a higher number and less-linear polymers, i.e., three dimensional polymers of small particle size, and these give, like bentonite, a stable structure different from that of the acid gels. This is somewhat analogous to the known effect of acid and alkali on the condensation of phenolic resins although the processes are dissimilar. At higher temperatures the peptizing effect of the alkali becomes greater and reduces the Young's modulus.

The above mechanism is in accord with the more elastic recovery of the acid gels when the load is removed and with the more rapid syneresis and shrinkage of alkaline gels as well as the marked differences in optical properties.

Houwink (5) cites the observations of Kowalski that the modulus of glass decreased with the temperature whereas Sosman (15) reported an increase. The latter differences are not analogous to those indicated in the present work, in that the experiments on glass were carried out on specimens formed at the same temperatures whereas our results were obtained with samples kept at the recorded temperature throughout the whole gelation period.

It is to be expected that if the medium is made more alkaline, the predominance of cross linkages would no longer compensate for reduced polymer size and the modulus would accordingly decrease. Measurements on more alkaline gels are therefore suggested. Some anomalous results were obtained with the acid gels at higher temperatures. It might be expected that at a certain temperature thermal vibration might cause breaking of the loosely linked structures in the acid gels and cause a decrease in the modulus values. The extension of the study to higher temperatures is desirable.

Acknowledgment

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LIGHT-SCATTERING APPARATUS AND TECHNIQUES FOR MEASURING MOLECULAR WEIGHTS OF HIGH POLYMERS¹

BY H. J. HADOW, H. SHEFFER, AND J. C. HYDE

Abstract

Apparatus is described for the measurement of small amounts of scattered light, dissymmetry of radiation, depolarization, and very small refractive index differences. Methods of calibration are critically examined. Benzene was adopted as a turbidity standard. Measurements were made on fractionated polystyrene of known molecular weight and on bovine serum albumin solutions. Values of the reduced intensity for benzene were obtained:

$$R = 33.4 \times 10^{-6} \text{cm.}^{-1} \text{ at } 25^\circ \text{C. and } \lambda = 4358 \text{ \AA, and}$$

$$R = 12.4 \times 10^{-6} \text{cm.}^{-1} \text{ at } 25^\circ \text{C. and } \lambda = 5461 \text{ \AA.}$$

Degree and sources of error are discussed

Debye (7, 8) has developed the theory of light-scattering in solutions and has produced an equation that relates the molecular weight of the solute to experimentally obtained values of turbidity, refractive index increment, and concentration. This equation, in its most popular form, is

$$II \frac{c}{\tau} = \frac{1}{M_2} + 2Bc, \quad (1)$$

where c is the concentration in grams per milliliter, τ is the turbidity or extinction coefficient in cm.^{-1} , M_2 is the weight-average (16) molecular weight of the solute, B is the constant that is used as a measure of deviation from ideality in the van't Hoff osmotic pressure equation and

$$II = \frac{32\pi^3}{3} \frac{n_0^2}{N\lambda^4} \left(\frac{dn}{dc} \right)^2,$$

where n_0 is the refractive index of the solvent, N is Avogadro's number, λ is the wave length of the incident light and $\frac{dn}{dc} = \frac{n - n_0}{c}$ for dilute solutions, n being the refractive index of the solution.

Several methods for measuring τ and $\frac{dn}{dc}$ have been described in the literature (e.g., 3, 9, 12, 26, 27, 28). This article deals with a few innovations and improvements that have been made in the apparatus and techniques. The main objective, however, will be to point out the difficulties that have been encountered, in the hope that others who wish to construct this type of equipment may avoid many time-consuming incidental investigations.

The Measurement of τ

For fairly turbid solutions, the extinction coefficient may be determined directly by transmission measurements, using Lambert's law. The use of the Beckman spectrophotometer for such measurements is discussed below under

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"Calibration". The turbidity of dilute solutions of most polymers is too low to be measured in this way since the difference in transmission between solvent and solution is very small. The easiest way to determine these turbidities is to measure the light scattered at right angles to the incident beam by the solution and by the solvent. The turbidity determined in this manner must be corrected for the effect of intramolecular interference when the length of the solute particles exceeds $\frac{\lambda}{20}$ (16, 21, 28).

The measured turbidity contains a contribution due to fluctuations in orientation of the molecules. This may be calculated if a measurement of the depolarization is made. The depolarization $\rho = \frac{H}{V}$, where H is the horizontal component and V the vertical component of the scattered light when the incident light is unpolarized. The depolarization has been neglected in Equation (1), but for accurate work and especially for large anisotropic molecules the molecular weights obtained from this equation must be corrected by multiplying by the inverse of the Cabannes factor, $\frac{6 + 6\rho}{6 - 7\rho}$. In most cases this reduces the value obtained for the molecular weight by less than 10%. For certain solvents (e.g., benzene and toluene) the depolarization must be corrected for the contribution of the solvent (11).

When the dimensions of the solute particles exceed $\frac{1}{20}$ of the wave length of the incident light, interference between the light waves scattered from different parts of the macromolecule brings about a change in the shape of the radiation envelope. More light is then scattered in the forward than in the backward direction (16). This causes the measured turbidity to be lower than the true value. The correction factor may be calculated if the dissymmetry (i.e., the ratio of the forward to backward intensities at equal angles about 90°) is measured. The theoretical variation of intensity with angle has been worked out for solute particles in the shapes of rods, spheres, or random coils (9, 16, 28). If the polymer under consideration is known to fit one of these models, the correction factor can be accurately obtained from the dissymmetry data and may increase the measured turbidity by over 100% in some cases (21). The length of the molecule can also be calculated from dissymmetry data (10, 16, 21). A satisfactory apparatus for obtaining molecular weights of large polymer molecules by light-scattering must, then, provide facilities for the measurement of (1) intensity of light scattered at right angles to the incident beam, (2) dissymmetry of the scattered radiation, and (3) depolarization of the light by the solution.

Light-Scattering Apparatus A

(i) Optical System

A schematic diagram of the apparatus is shown in Fig. 1. The light source is a General Electric AH-4 mercury lamp cooled by a small fan. By

means of a lens an image of the source is focused on a diaphragm with an opening of about 2 mm. diameter. A second lens is placed at a distance equal to its focal length from the diaphragm to give a beam of substantially parallel light.

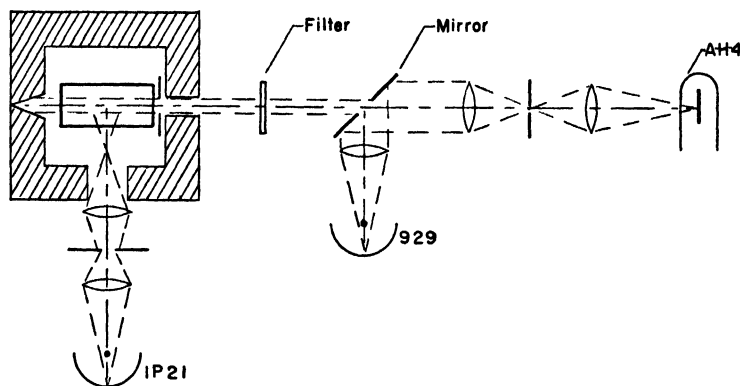


FIG. 1. Light-scattering apparatus A.

The light-beam then passes through color filters. The 5461 \AA line was isolated as closely as possible by one set of filters, the 4358 \AA line by another. The response of the system to different wave lengths is affected by (a) the color filters used, (b) the intrinsic response of the photosensitive surface, and (c) the relative intensity of the different wave-length bands in the light from the source. For the 5461 \AA line a Corning filter No. 3484 is used to eliminate all wave lengths below 5200 \AA , with a No. 5120 filter to eliminate the strong band at 5770 \AA in the mercury spectrum. This filter combination would pass light of wave lengths greater than 6000 \AA , but the S-4 surface of the photomultiplier that was used to measure scattered intensity is decreasingly sensitive to increasing wave length in this region. The source produces a continuous spectrum of intensity about 2 to 3% of that of the 5461 \AA line. It is estimated that the system is influenced by the continuous spectrum over the range 5200 to 5700 \AA , which is passed by the filters, but the response is less than 3% of that caused by the 5461 \AA line. The effect of other wave lengths is negligible. For the 4358 \AA line, Corning filters No. 5113 and No. 3389 are used.

It was desired to reflect a portion of the incident beam onto a 929 phototube linked to the photomultiplier circuit in such a manner as to compensate for fluctuations in the output of the lamp. The circuit is described in detail below. At first the simple procedure, adopted by Doty, Wagner, and Singer (12), of placing a pair of parallel glass plates at 45° to the beam was used. It was found, however, that this partially polarized the beam, necessitating, as a compensator, the insertion of a "depolarizer" of two further plates at 45° , but reflecting on an axis at 90° from the first pair. Since these plates decreased the intensity of the beam considerably, the method of Zimm (29) has recently been adopted. This involves simply the use of a silvered glass plate with a hole in the center. Most of the beam passes through the hole, and the small fraction striking the plate is reflected onto the 929.

The main portion of the beam then passes through a hole 1 cm. square into the cell chamber, which is a thermostatically controlled box of inside dimensions 4 by 4 by 6 in., the outside dimensions being $1\frac{1}{2}$ in. greater all around. Water from a thermostat can be pumped through the walls, bottom, and lid of the box. After passing through the solution cell the beam is finally trapped in a blackened cone.

The scattered light is picked up by a lens and focused on a slit slightly smaller than the photosensitive surface, an image of the slit being focused by an additional lens onto the photomultiplier. The light must not be focused directly to a small spot on the sensitive surface, as this causes rapid local fatiguing and nonlinearity of response. In addition, any slight movement of the parts would move the spot on the sensitive surface; this is to be avoided, as the sensitivity varies over the surface. The latter point has been emphasized recently by Zimm (29).

When using solutions scattering large amounts of light, the photomultiplier is protected by the use of a 1.3 neutral density filter in the incident beam. By calibration, both on the apparatus and on a spectrophotometer, the filter reduced the intensity by a factor of approximately $1 : 24$ for $\lambda = 5461 \text{ \AA}$, and $1 : 38$ for $\lambda = 4358 \text{ \AA}$.

For the measurement of depolarization, polaroid disks can be inserted in the paths of the incident and scattered light beams. With suitable photomultipliers (see below) much more accurate determinations of depolarization at low light intensities can be made than by visual methods such as the Cornu method (11).

(ii) Cells and Dissymmetry Device

Rectangular glass cells of dimensions 4 by 2 by 8 cm. were used. For measurements of 90° scattering alone, these cells could be used with the 4 cm. sides parallel to the incident beam. For use with the dissymmetry device, however, it was necessary to cement a glass slide on the 4 by 2 cm. opening, drill an opening in one of the 8 by 2 cm. sides and use the cell with the 8 cm. sides parallel to the incident beam. There was no difficulty in obtaining suitable cements for aqueous solutions, but for organic solvents such as benzene the many cements tried proved very unsatisfactory except for a gum arabic – sucrose – water cement suggested by Dr. Marcel Rinfret (24).

For the measurement of dissymmetry, a brass block carrying two small front surface mirrors (Fig. 2) was used. The block fitted snugly on two pins in a position parallel to the cell and about 1 cm. in front of it. In one position the angle of view in air was 43° from the direction of the incident beam; with the block turned end over end the angle was 137° . Allowing for refraction at the cell wall, the angles with benzene in the cell were 63° and 117° . A diaphragm was placed so that only light from the center portion of the second mirror was viewed by the photomultiplier.

The cell holder, comprising a rectangular recess for the vessel with inlet and exit diaphragms, was of sheet brass soldered to a brass plate. This assembly, together with the dissymmetry block, could be removed from the thermo-

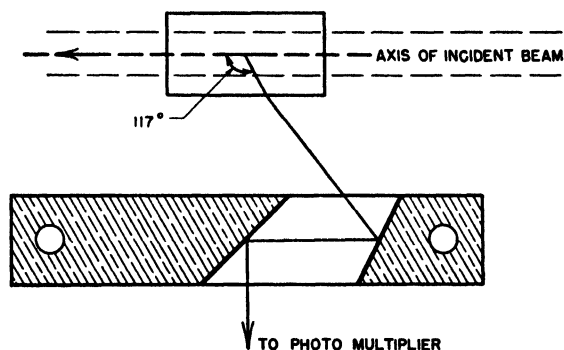


FIG. 2. Dissymmetry device.

statically controlled box. All interior surfaces were painted flat black. Additional shielding around the cell holder was found to be necessary to eliminate stray light, which was particularly likely to interfere with the dissymmetry measurements. With clean benzene in the cell, dissymmetries varying by 1 to 2% from 1.0 were obtained. Small variations were due to imperfections in the cell walls and the degree of cleanliness of the surface.

(iii) The Photoelectric System

Since it is desirable to use a photomultiplier with an S-4 surface for greatest sensitivity in the blue-green region, one has to choose between the 931-A and 1P21 photomultiplier tubes. The latter is much more expensive, but has definite advantages, particularly in so far as stability and low dark current are concerned. Comparison between three 1P21's and five 931-A's is given in Table I. The last column gives the measured depolarization of benzene

TABLE I
CHARACTERISTICS OF PHOTOMULTIPLIERS

Tube No.	Sensitivity relative to 1-P21-A	Dark current, $\times 10^9$ amp.	ρ for C_6H_6
1P21-A	1.00	3	0.42
1P21-B	0.32	3	0.44
1P21-C	0.42	3	0.42
931-A-1	0.14	40	0.37
931-A-2	1.09	70	0.38
931-A-3	0.37	20	0.38
931-A-4	0.07	10	0.34
931-A-5	0.17	90	0.40

for each tube. It may be seen from this table that the sensitivities of the best 1P21 and the best 931-A are about the same, but in every case the dark currents of the 1P21's are much lower than those of 931-A's. In this regard it is necessary to illuminate the new tubes strongly for some time until the dark current is reduced to a low steady value. Even with this precaution there are always some fluctuations in the dark currents of the 931-A's.

A value of 0.420 is given by Cabannes (4) for the depolarization of benzene. It appears that the 1P21's duplicate this value fairly closely, while the 931-A's give varying low values indicating that they are more sensitive to vertically than horizontally polarized light. This is particularly difficult to understand, since, according to Johnson (14), 1P21's are the selected 10% of the 931-A's having low noise and stable sensitivity.

All phototubes fatigue or recover during use, depending on the intensity of light being measured. This necessitates repeated reference to turbidity standards in light-scattering work. Since the drift increases with output, it was found a desirable precaution to keep the output below $5\mu\text{a.}$, which is considerably lower than the figure suggested by Engstrom (13).

For the satisfactory use of a photomultiplier in the light-scattering apparatus it is necessary to have a supply of regulated high voltage to be applied to the stages of the multiplier and also to eliminate or compensate for fluctuations in intensity of the light source. The basic circuits to meet these requirements were designed by Dr. R. B. Harvey of these laboratories and are shown in Fig. 3.

The high tension voltage regulation embodies the principles of Bereskin (1). V_4 consists of five type 991 voltage regulating tubes which draw about 1 ma. The bridge $R_6R_7R_8$ draws approximately $\frac{1}{2}$ ma. The approximately 1000 v. are divided up between the stages of the multiplier, slightly over 100 v. being applied to each stage except the last one. To increase the stability only 50 v. are applied to the last stage.

Fluctuations in the intensity of the light source cannot be eliminated entirely by control of the voltage applied to the lamp. Variation in the temperature of the lamp, local hot spots, and aging are additional sources of fluctuations. The 929 photocell was used to compensate for these by adjusting the amplification of the photomultiplier (19) in the manner shown in Fig. 3. The 929, which receives a small amount of light from the incident beam, was connected between dynode 4 and dynode 2 of the photomultiplier. Dynode 4 was connected to the arms of R_{19} through a 5 meg. variable resistor R_{20} . Now, if the voltage of one dynode is plotted against the output of the photomultiplier a peaked curve is obtained owing to defocusing of the electron beam at voltages greater or lower than the optimum. If the voltage of the dynode in question is set at such a point that an increase of voltage causes the over-all amplification of the photomultiplier to increase while at the same time the increase of voltage

on the dynode causes defocusing and a decrease of the output, then the net output will tend to remain stationary. In this case it was found experimentally that varying the voltage on dynode 4 gave the most satisfactory results. R_{19} allows the voltage on dynode 4 to be put on the descending portion of the output-voltage defocusing curve. The flow of current in V_2 causes the dynode end of R_{20} to become negative. Now an increase in the intensity of the light

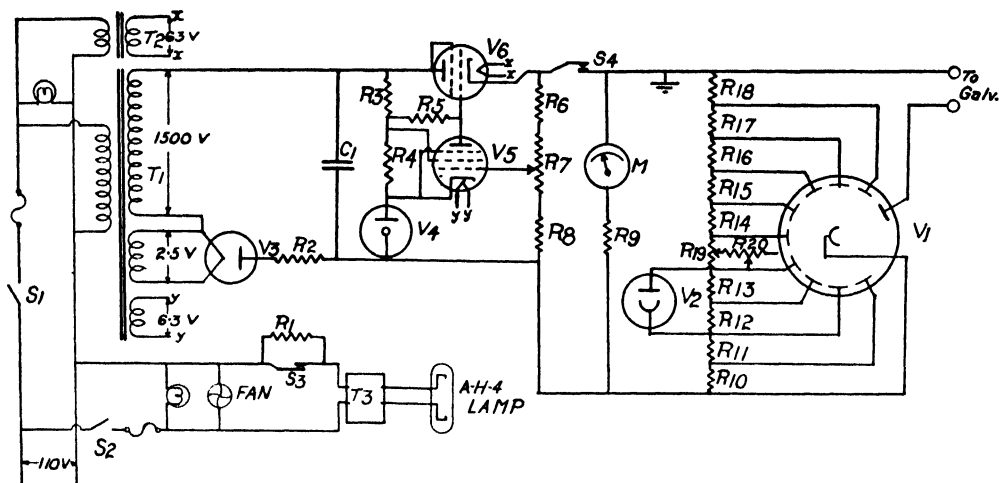


FIG. 3. *Photoelectric system.*

Parts list

V1	1P21 Photomultiplier	R1	3 ohms, 7.5 w.
V2	929 Phototube	R2	50k ohms, 10 w.
V3	2X2 Rectifier	R3	1 megohm, 2 w.
V4	5-991 Voltage regulators	R4	250 k ohms, 1 w.
V5	6SJ7	R5	2 meg.
V6	6V6	R6	3 meg.
T1	Hammond 215 C.R.O. transformer	R7	100 k ohm pot.
T2	Hammond 167C transformer	R8	1 meg.
T3	G.E. Autotransformer for AH4 lamp	R9	2 megohms
S1	H.T. switch	R10-R17	100 k ohms
S2	Mercury lamp switch	R18	50 k ohms
S3	Push button—normally closed	R19	100 k pot.
S4	Microswitch—normally open	R20	5 meg. pot.
M	Meter 0-1 ma.	C1	1 μ f. 2000 W.V.

source causes the output of V_1 as a whole to increase. Simultaneously it causes the current through V_2 and R_{20} to increase; this makes the dynode end of I_2 more negative and forces the amplification down. When the effects are balanced, fluctuations of the light source have a minimum effect on the output. The circuit was adjusted so that a 10 v. change in the light source supply had a negligible effect on the output reading. When S_3 is opened R_1 causes a drop of about 6 to 8 v. in the supply voltage and aids in setting R_{19} and R_{20} to compensate for fluctuations in light source intensity. These settings rarely have to be changed during operation.

The microswitch S_4 breaks the circuit automatically when the lid of the cell chamber is opened. This eliminates possible overloading of the photomultiplier and galvanometer by admitting external light with the high tension still applied.

The output of the photomultiplier is measured directly on a Rubicon galvanometer with a 100 mm. scale and a sensitivity of $0.005 \mu\text{a. per mm.}$ An Ayrton shunt is used when necessary with the larger currents. The sensitivity of the instrument in terms of turbidity is about $1 \times 10^{-6} \text{cm.}^{-1}$ per mm. galvanometer deflection when using photomultiplier 1P21-A.

Light Scattering Apparatus B

For measuring the dissymmetry of large molecules it is desirable to use angles closer to the incident beam than was possible with Apparatus A (20). It is also desirable to measure the dissymmetry at more than one angle, and at more than one wave length, to determine whether a satisfactory model has been chosen for the molecule. For these reasons a second apparatus (B) was designed as shown schematically in Fig. 4.

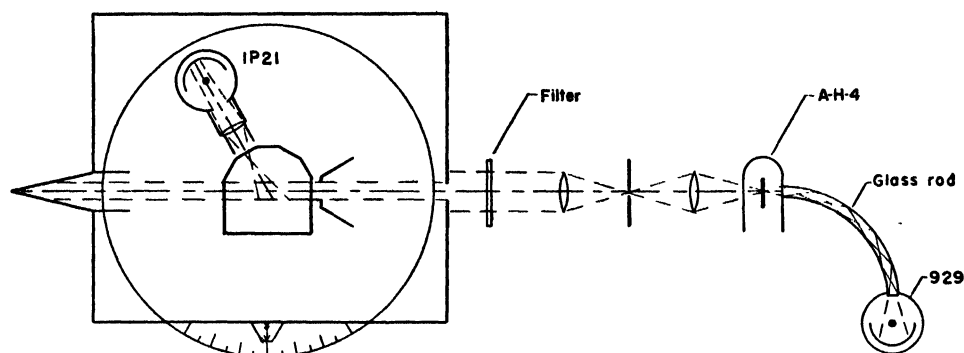


FIG. 4. *Light-scattering apparatus B.*

The cell, made by Klett, was of optical glass fused at the corners. The viewing angles were $33, 60, 90, 120,$ and 147° . Each of the viewing faces was 12 mm. wide, the entering and exiting faces were 30 mm. wide, and the back face close to 50 mm.; the height was 100 mm. The cell was mounted on a platform about which the photomultiplier could be rotated so that the scattered light at each angle was viewed at 90° to the face. Thus no correction was required for the refractive index of the liquid. Direct transmission measurements could also be made. The photomultiplier was mounted on a rotating arm attached to a divided circular scale. Part of the scale protruded from a false bottom in the blackened box containing the cell and multiplier.

The optical system was similar to that in Apparatus A. A 6 mm. square slit about 4 cm. from the cell defined the light beam and it was found necessary to insert a slightly larger slit close to the cell in order to remove any divergent portion of the beam.

This apparatus could be connected into the electrical circuit of Apparatus A by means of a 12-pin Jones plug. In this case the AH-4 lamp was enclosed in a water-cooled jacket from which a portion of the light was led off to a 929 phototube by means of a bent glass rod.

Calibration and Measurements

Attempts were made at first to calibrate the apparatus by means of a magnesium carbonate surface at 45° to the light beam as described by Stein and Doty (28). The size of the opening through which the photomultiplier views either the illuminated area of the block, which is of a size fixed by the width of the beam, or the luminous zone in the solution, which is limited only by the length of the cell, is obviously extremely critical. In addition there is a certain amount of specular as well as diffuse reflection from the block at this angle.

This method was then discarded in favor of that used by Doty, Affens, and Zimm (10) in which the turbidity standard was a solution of polystyrene in ethyl methyl ketone which was calibrated on a Beckman spectrophotometer. It is necessary to use solutions that exhibit no dissymmetry; this means that the molecular weight of the polystyrene used should not be much greater than 50,000. Great care must be used in obtaining the matching factors of the cells (25) and in the handling of the solutions. Since the turbidities are fairly low it is very easy to introduce errors of the order of 10% in turbidity by errors of 0.2% in transmission on the Beckman. In addition, it was found most difficult to remove the last "motes" from the fairly large volumes of solution required, either by centrifuging or by filtering through fine or even ultrafine filters. Any handling, particularly pouring from one vessel to another, introduced many dust particles. It is necessary to make a correction for absorption of the light over the path traversed in the cell of the light-scattering apparatus. Since the standard has a much higher turbidity than the solutions to be measured, this correction may be of the order of 5%. Another difficulty was a change of the ethyl methyl ketone with time. It is a desirable solvent to use in these measurements because the $\frac{dn}{dc}$ for polystyrene in ethyl methyl ketone is very high. However, the solvent polymerizes and readily develops a greenish cast that is difficult to remove. In any case, such solutions calibrated on the Beckman were found to have turbidities 10 to 30% too high when compared with benzene as a standard of turbidity on the light-scattering apparatus.

It would appear, therefore, that a solvent of relatively high scattering power such as benzene or carbon disulphide would serve as the best standard of turbidity. The turbidities of these solvents have been measured with a reported accuracy of about $\pm 6\%$ (4, 5, 6, 22). Such values can also be obtained using the light-scattering apparatus if a material of known molecular weight is used as a reference standard. Carbon disulphide has the higher turbidity and was found satisfactory for use with green light, but not with

blue, since it is apparently sensitive to light of lower wave length (4). Benzene was chosen as the standard, since much of the work planned for the apparatus had to do with benzene solutions. Reagent grade benzene was redistilled twice through a packed column, the middle fraction being kept each time. The product was found to be quite free from motes when observed at angles close to a beam of light passing through it. A suitable quantity of the solvent was sealed in appropriate cells for use in both light-scattering apparatus *A* and *B*.

When using a solvent in this manner as an absolute standard of turbidity, it is necessary to learn if the cell itself contributes appreciably to the light scattered. This cannot be determined from measurements on the empty cell because internal reflections then make the value unrepresentative. An estimate of the contribution may be obtained by viewing the cell filled with "clean" water which has a very low scattering power (4). Comparing the scattering power of benzene with that of water in the present equipment it was estimated that any contribution of the cell was below 2% of that of benzene. Imperfections in the cell walls, however, caused variations of the order of 2% in the readings for benzene in different cells. In this regard it was found most important to highly polish the cell walls, as any microscopic contamination picks up dust particles which reflect light to the multiplier. It should be emphasized that the size of the cells, the position of the beam through the cells, and the viewing angles were chosen to avoid reflections from corners and interference from the spot that is brightly illuminated by the incident beam.

Having adopted benzene as a turbidity standard, the technique of measuring the turbidity of unknowns must now be considered. In this connection the most important point is the "cleaning" of the solutions since it is obvious that dust particles increase the turbidity and especially the dissymmetry. Since large cells were deliberately chosen for the reasons mentioned above, a minimum of 40 cc. of solution was required in each cell. It has also been previously noted that cleaning such amounts of solution by filtering was found quite unsatisfactory. Not only is it difficult to remove fine motes by this method, but in addition an analysis of the solution is required after filtering. For example, in one extreme case a Berkfeld candle filter removed over 75% of the polymer present in solution. Even small sintered glass filters removed as much as 10%. For the solvents themselves ordinary distillation proved very satisfactory in the case of organic solvents. Water, however, presents a much more difficult problem and it was found that freshly distilled water from a good still looked very "dirty" when examined in a Tyndall beam.

Of all the methods tried, only the one described by Bhagavantam (2) was found at all successful in removing the "motes" from water. Water was distilled from a warm bulb to a cold one under vacuum, and after rinsing the cold bulb returned again for repeated distillations. Air was slowly allowed into the warm bulb, the tube connecting the bulbs broken and the purified water poured into the light-scattering cell. The method was found to be quite tedious and not always completely successful.

The following operating procedure was finally adopted as being the most satisfactory of those investigated. A Sorvall SS-1 angle centrifuge (12,000 r.p.m.) was used to clean the solutions. The ordinary round-bottomed tubes provided with the instrument are not very satisfactory for this work because the sediment is easily stirred up by convection currents when the centrifuge is stopped and particularly by any jarring on removal of the tubes. To diminish this effect the 15 cc. heavy-walled Pyrex tubes were drawn down and sealed to a 1.5 mm. capillary tube about 3 cm. long. The resulting tube, which was very similar in appearance to a Hopkins Vaccine Tube, had a capacity of about 6 cc. Polyvinyl alcohol caps were made for use with organic liquids. For turbidity measurements, the eight tubes were usually filled with a 1% solution and, after centrifuging, 1 cc. portions were removed by pipette from each tube in turn to be added to the 40 to 50 cc. of distilled solvent in the light-scattering cell. With this procedure eight points in the concentration range 0.02 to 0.2 gm. per 100 cc. could be obtained. The centrifuge was kept running between each measurement. Readings for benzene in the standard cell were taken before and after each solution measurement. To avoid evaporation, glass slides in which an 8 mm. hole had been drilled were cemented to the cells and the hole plugged with a suitable cap. Although the volumes of solvent used were large, the actual amount of polymer necessary for the measurements was quite small. To facilitate calculations it was found advisable to set the galvanometer reading for benzene at a predetermined value by adjusting the potentiometer R_7 (Fig. 3). This galvanometer reading then corresponded to the turbidity value for benzene and the reading for the unknown yielded the uncorrected turbidity directly after subtraction of the contribution of the solvent. Dissymmetry and depolarization corrections were obtained in the manner previously described.

The first check on the apparatus was to measure the ratio between the scattered intensities for carbon disulphide and benzene. Ratios of 4.3 to 4.4 were obtained which may be compared with the values of 4.38 obtained by Martin (17), 4.54 by Martin and Lehman (18) and 4.12 by Krishnan (15).

It was necessary to check the validity of using benzene as a standard by the use of material of known molecular weight. For this purpose a sample of polystyrene was prepared by polymerization at 175° C. Fractionation was carried out by the standard method of precipitation from very dilute solutions. Each fraction was reprecipitated and one of the fractions was carefully refractionated for this work. The intrinsic viscosity of the final fraction differed from that of the previous one by only 0.5%; this indicated that the molecular weight distribution must be very narrow. From the very accurate osmotic pressure measurements of Dr. L. A. McLeod of the National Research Laboratories, the molecular weight of the final narrow middle fraction was determined to be 141,000. Benzene solutions of this fraction were then examined at 25° C. on both light-scattering apparatus *A*

and B at $\lambda = 4358 \text{ \AA}$ and 5461 \AA . Results from a number of experiments were averaged; this gave $\left(\frac{c}{\tau_{\text{rel}}}\right)_{c=0} = 1.02 \times 10^{-3}$ for the blue line and 0.946×10^{-3} for the green line. The values for τ_{rel} must be multiplied by the corresponding turbidity of benzene for conversion to absolute values and also corrected for dissymmetry.

Values of the turbidity of benzene at 25°C . for the 5461 \AA line do not appear to be available in the literature. However for the 4358 \AA line at 24° Peyrot (23) gave a value of $(34.8 \pm 2.3) \times 10^{-6}$ for the reduced intensity R , corresponding to $\tau = 5.83 \times 10^{-4} \text{cm.}^{-1}$ $\left(\tau = \frac{16}{3} \pi R\right)$. The variation of the reduced intensity of benzene with temperature is given by Cabannes as an increase of 0.7% per degree, so that the temperature correction may be neglected here. This number for the turbidity of benzene may then be used to change the τ_{rel} 's obtained for the polystyrene solutions into absolute turbidities. To obtain the dissymmetry correction the measured dissymmetries of the polystyrene solutions were plotted against concentration and a value of 1.08 was obtained by extrapolation to infinite dilution. The measured turbidity must then be increased by 4% , assuming a random coil model for the polystyrene (10, 28). Inserting the corrected value for $\left(\frac{c}{\tau}\right)_{c=0} = 1.685$ in Equation (1) along with the determined value of $\frac{dn}{dc} = 0.106$ (see below), a molecular weight of $155,000$ was obtained. This must now be reduced by 5% because of the depolarization correction, the measured depolarization for very dilute solutions being $\rho = 0.027$. A final value of $147,000$ (as compared with $141,000$ by osmotic pressure) was obtained. Excluding experimental error, these values should be the same if the assumption is made that the molecular weight distribution of the polystyrene fraction is so narrow that the number-average and weight-average molecular weights are nearly identical.

It is probable that the value obtained by osmotic pressure measurements for the molecular weight of the polystyrene fraction is more reliable than the number for the reduced intensity of benzene used in the above calculations. It is therefore desirable to recalculate the latter from the present data. Assuming $141,000$ to be the correct molecular weight, R for benzene at 25°C . and $\lambda = 4358 \text{ \AA}$ should equal $33.4 \times 10^{-6} \text{cm.}^{-1}$. Cabannes (5) has calculated a value of R at 15°C . for this wave length; his figure when corrected to 25°C . is approximately 29.3×10^{-6} . This is considerably lower than Peyrot's value (34.8×10^{-6}) and the one determined in this manner from the light-scattering data. Working backwards from the measured $\left(\frac{c}{\tau_{\text{rel}}}\right)_{c=0}$ for $\lambda = 5461 \text{ \AA}$ and assuming that $141,000$ is the correct molecular weight, a value for the reduced intensity of benzene at 25°C . and for this wave length was obtained, $R = 12.4 \times 10^{-6} \text{cm.}^{-1}$. Zimm (29) has estimated a value

of 13×10^{-6} for R at 20°C . and $\lambda = 5460$ by using the data of Peyrot and the value of $R = (10.7 \pm 0.55) \times 10^{-6}$ for $\lambda = 5440 \text{ \AA}$ and a temperature of 15°C . determined by Cabannes and Daure (6). This is equivalent to $R = 13.4 \times 10^{-6}$ at 25°C . and $\lambda = 5460$. This estimate is considerably higher than our calculation of $R = 11.2 \times 10^{-6}$ from the same data. The value determined experimentally from the light-scattering data is probably more reliable than either estimate and corresponds to $\tau = 2.07 \times 10^{-4} \text{cm}^{-1}$ ($t = 25^\circ \text{C}$. and $\lambda = 5461 \text{ \AA}$).

The measurements were extended to aqueous solutions of crystalline bovine serum albumin (from the Armour Laboratories). In this case the solvent contained a considerable number of small motes, but it was possible to obtain small amounts of clean 1% solutions of the protein by centrifuging in a cold room at 5°C . The increment in turbidity obtained on addition of the solution to the solvent must then be due only to added solute and the results should be reliable. For $\lambda = 5461 \text{ \AA}$, $t = 25^\circ \text{C}$., and using the τ previously determined for benzene as a standard, a value of $\left(\frac{c}{\tau}\right)_{c=0} = 3.73$ was obtained. Insertion of this in Equation (1) along with $\frac{dn}{dc} = 0.187$ (22) yielded a value for the molecular weight = 70,000 (accepted value 69,000). The dissymmetry and depolarization corrections were found to be negligible. This good agreement supports the reliability of the calculated τ of benzene and the osmotic pressure measurements on the polystyrene.

In one experiment the albumin solution was filtered through a fine Pyrex filter. Measurements with this solution indicated a molecular weight increasing from 78,000 to 88,000 during the course of an afternoon. Continued increase of turbidity and dissymmetry was due to the growth of micro-organisms indicating another source of error with aqueous solutions.

The Measurement of $\frac{dn}{dc}$

For most high polymers $\frac{dn}{dc}$ is of the order 0.1 to 0.2. The usual practice is to measure the refractive index difference between a 1% solution and the solvent (0.001 to 0.002) and make the reasonable assumption that the difference varies directly with concentration. Since the $\frac{dn}{dc}$ term is squared in Equation (1), an error of one in the fifth decimal for $(\Delta n)_{1\%} = 0.001$ means a 2% error in molecular weight. The extreme limit of accuracy of the Pulfrich Refractometer is $1 \text{ to } 2 \times 10^{-5}$. To obtain this accuracy several modifications and precautions are necessary.

First of all, the same sample of solvent must be used in making up the solution and in the measurements. Appreciable differences in refractive index due to traces of impurities such as water were found between samples of reagent benzene from different bottles. Another precaution is to ensure that solvent

and solution are at the same constant temperature. It is desirable to construct a jacket to fit over the cell of the refractometer and circulate the thermostat water through it as well as the cell holder. The greatest difficulty with the differential cell is that the liquids creep, by capillarity in the corners, from one side to the other. It was found necessary to seal one side from the other with a specially designed polyvinyl alcohol lid in which there were holes with caps for filling. It is necessary to take the average of many readings for each of several fillings of the cell.

It was planned to use the light-scattering apparatus to investigate polymeric aluminum soaps which had been previously studied by means of osmotic pressure and viscosity measurements by Sheffer (26). For these compounds in benzene $(\Delta n)_{1\%}$ is of the order of 0.0004, so that the accuracy of the Pulfrich is obviously insufficient. Greater accuracy can be obtained with the use of interferometry or of specially designed differential refractometers. The differential refractometer designed for this work was similar in principle to that of Debye (9) and Bryce and Speiser (3). The principle is magnification by an optical lever of the slight shift in a beam of light due to refraction at the interface between solvent and solution.

The main feature of the instrument shown schematically in Fig. 5 is that the parallel monochromatic beam of light is refracted four times by making

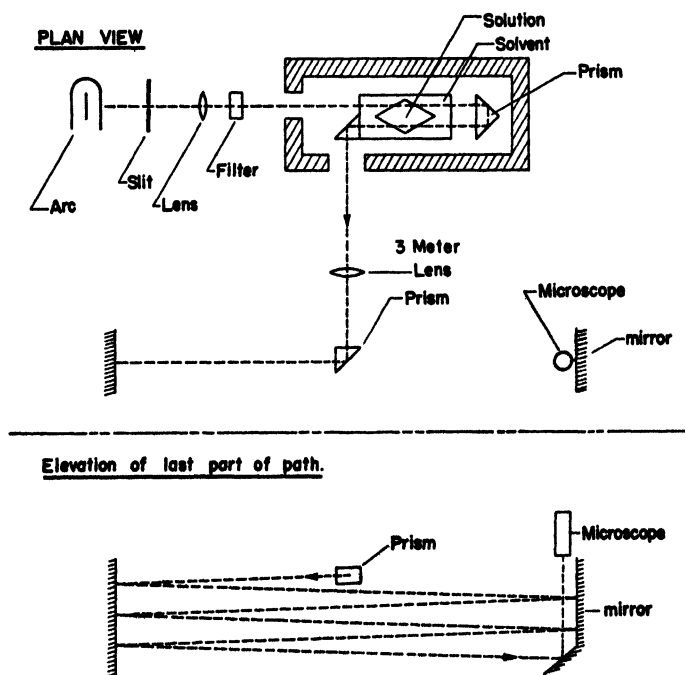


FIG. 5. Differential refractometer.

use of a diamond shaped cell and reflecting prisms. This cell is made of stainless steel with glass windows cemented over the holes; the refracting angle is 130° . The cell is filled with 6 cc. of solution and cemented into a

rectangular glass cell containing solvent. This cell is placed in a holder in a box through the walls of which water is circulated from a thermostat. It is necessary to use a good adjustable slit as the source. An image of this slit is formed at the extremity of a 3 m. optical lever and its deflection, from the zero with no cell present, is measured by means of a traveling microscope micrometer. The space required is reduced by reflecting the beam back and forth between two parallel front surface mirrors.

For calibration of this apparatus a 4% solution of cyclohexane in benzene was prepared and the desired refractive index increment obtained on the Pulfrich refractometer. The deflections for several dilutions of this solution were measured on the differential refractometer. Fig. 6 shows the sensitivity

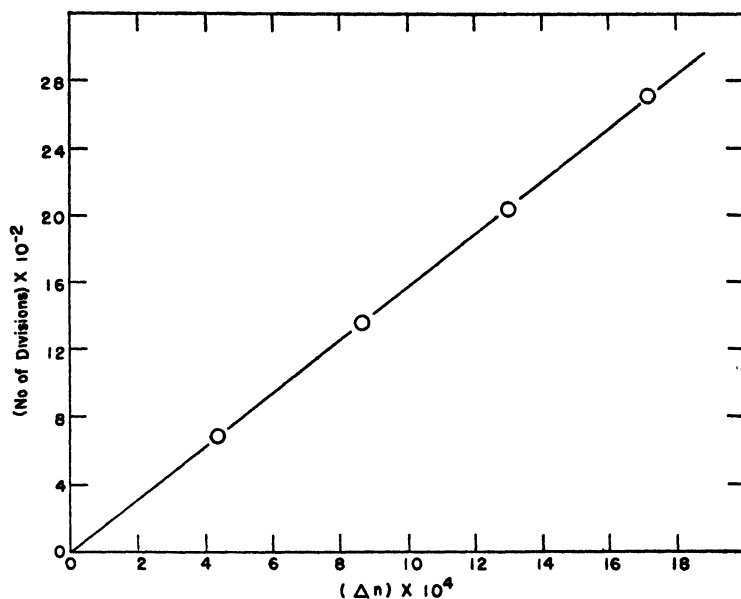


FIG. 6. Calibration and linearity of differential refractometer.

and linearity of the apparatus. One division on the micrometer corresponds to a refractive index difference of about 6×10^{-7} . It was necessary to correct the zero for a small shift produced when both cells were filled with solvent. This was because the faces of the rectangular cell were not exactly parallel to one another or perpendicular to the beam. Because of the method used in mounting the components in this apparatus it was found that room temperature variations also caused a small shift in the zero, so that it had to be redetermined after each reading with the cell in position. Two hours was required for the attainment of true temperature equilibrium and readings were continued through the course of the day and finally averaged.

Discussion

The accuracy of the molecular weights obtained by the light-scattering method is limited by the accuracy of the turbidity standard as well as the

experimental errors involved in the measurements. In cases in which it is possible to get solvent and solutions relatively "clean" the latter error should be less than $\pm 5\%$, but, as a rule, for water and aqueous solutions this error is increased, particularly when dissymmetry measurements are required. The error in the directly measured turbidity of benzene is said to be about $\pm 6\%$ (6, 23), while errors in using other methods for calibration of the light-scattering apparatus are considerably greater. It would appear, therefore, that until more accurate measurements of the turbidity of benzene or other standards are made, a possible error of about $\pm 10\%$ must be admitted for molecular weights obtained by light-scattering methods which are comparative in nature.

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THE EFFECT ON REACTION RATES CAUSED BY THE SUBSTITUTION OF C¹⁴ FOR C¹²¹

I. THE ALKALINE HYDROLYSIS OF CARBOXYL-LABELED ETHYL BENZOATE

BY WILLIAM H. STEVENS AND RICHARD W. ATTREE²

Abstract

A study of the alkaline hydrolysis of C¹⁴ carboxyl-labeled ethyl benzoate has shown that the substitution of C¹⁴ for C¹² changes the rate of hydrolysis of the ester. Ester molecules containing C¹⁴ hydrolyze at a slower rate than normal ester molecules. The ratio of the hydrolysis rate constants at room temperature has been found to be 0.86 ± 0.016 .

Introduction

In the past it has been assumed, in studies using tracer isotopes, that the labeling atoms are chemically indistinguishable from the more abundant normal atoms, except in the case of the hydrogen isotopes, and perhaps lithium. The small differences in the physical properties of compounds containing different isotopes of the same element which make it possible to concentrate isotopic species such as C¹³ and N¹⁵ in the form of C¹³O₂, C¹³H₄, and N¹⁵H₃, for example, were considered to have so little effect on normal reactions as to be negligible for ordinary tracer purposes. For instance, the equilibrium enrichment factor for the reaction $\text{HC}^{12}\text{O}_3^- + \text{C}^{13}\text{O}_{2(g)} \rightleftharpoons \text{C}^{12}\text{O}_{2(g)} + \text{HC}^{13}\text{O}_3^-$ at room temperature, is only 1.012.

Recently, however, it has been found in several laboratories that quite appreciable isotopic effects occur with both C¹³ and C¹⁴. Beeck and coworkers (1) were the first to note an effect, and found that the dissociation probabilities of the C¹²-C¹² and C¹²-C¹³ bonds of the molecule-ions formed from propane-1-C¹³ by electron impact differed by about 20%. Later (7) they subjected propane-1-C¹³ to pyrolysis at 500° C. and found an 8% more frequent rupture of C¹²-C¹² bonds than of C¹²-C¹³. Yankwich and Calvin (8) thermally decarboxylated singly carboxyl-labeled malonic and bromomalonic acids, and found that the C¹²-C¹² bond ruptured 12% more frequently than the C¹²-C¹⁴ bond in malonic, and 41% more frequently than the C¹²-C¹⁴ bond in the bromomalonic acid. It should be noted, however, that from a theoretical consideration of the isotopic effect to be expected in these cases, Bigeleisen (2) obtains values that are in disagreement with the experimental values and predicts a considerably smaller effect. Still more recently, Daniels and Myerson (4) hydrolyzed C¹⁴ labeled urea using the enzyme urease, and found that the carbon dioxide produced early in the hydrolysis had a noticeably higher specific activity than that produced late in the hydrolysis.

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A simple alkaline ester hydrolysis was chosen for the initial study of the effect of C^{14} substitution on reaction rates in this laboratory. The ester used was ethyl benzoate.

Discussion

If the rate of hydrolysis of carboxyl - C^{14} ester molecules were slower, for example, than that of normal C^{12} molecules, the first portion of acid produced in the hydrolysis of labeled ester would contain a smaller percentage of labeled molecules than were present in the ester before hydrolysis began. As hydrolysis continued, acid produced during any short period would contain an increasingly greater percentage of labeled molecules as the normal ester molecules were impoverished more rapidly than the labeled molecules. Very near the end of the hydrolysis the last portion of acid produced would have the greatest concentration of label. Over-all, the complete hydrolysis would show no isotopic fractionation, but total acid produced up to any time before complete hydrolysis would show a specific activity less than that of the acid as a whole.

It was considered that isotopic fractionation might occur only to a slight extent in hydrolysis. Preliminary experiments were therefore done, based on the foregoing reasoning, with a view to observing as large a difference in specific activity as possible. Consecutive samples of benzoic acid as it was produced in an hydrolysis of labeled ester were obtained, and their specific activities determined and compared. The trend in specific activity was noticeably upward, and the specific activity of the last sample of acid was some 20% higher than that of the first, showing that the labeled molecules did hydrolyze at a slower rate than the normal ester molecules. When this magnitude of difference was observed, it was decided to determine the effect more accurately in terms of relative reaction rates.

If an hydrolysis of an ester, a bimolecular reaction, is done with an excess of hydroxyl ion present, kinetically the reaction is first order.

Let

$$k = \frac{1}{t} \ln \frac{C_0}{C_0 - x} \quad (1)$$

and

$$k^* = \frac{1}{t} \ln \frac{C_0^*}{C_0^* - x^*} \quad (2)$$

be the integrated rate expressions for the hydrolysis of the normal and labeled molecules, respectively, where C_0 and C_0^* are the initial concentrations of ester and x and x^* are the concentrations of acid produced up to time t .

Let

$$C_0^*/C_0 = a, x^*/x = a', \text{ and } a'/a = r,$$

then

$$C_0^* = aC_0 \text{ and } x^* = a'x = arx.$$

Dividing (2) by (1),

$$\frac{k^*}{k} = \frac{1/t \ln \frac{C_0^*}{C_0^* - x^*}}{1/t \ln \frac{C_0}{C_0 - x}}$$

If the hydrolysis is allowed to proceed until $\frac{x}{C_0} = f$
then

$$\frac{k^*}{k} = \frac{\ln \frac{C_0}{C_0 - rfC_0}}{\ln \frac{C_0}{C_0 - fC_0}} = \frac{\ln \frac{1}{1 - rf}}{\ln \frac{1}{1 - f}} = \frac{\ln (1 - rf)}{\ln (1 - f)} \quad (3)$$

When $x^* \ll x$ and $C_0^* \ll C_0$, $\frac{x + x^*}{C_0 + C_0^*} \approx \frac{x}{C_0} = f$.

Further,

$$\frac{x^*}{x + x^*} \approx \frac{x^*}{x} = a', \text{ and } \frac{C_0^*}{C_0 + C_0^*} \approx \frac{C_0^*}{C_0} = a.$$

Therefore

$$r \approx \frac{\frac{x^*}{x + x^*}}{\frac{C_0^*}{C_0 + C_0^*}},$$

which is the ratio of the specific activity of the reacted fraction to that of the initial ester.

Thus the ratio of the reaction rates, for a first order reaction, may be determined readily if the initial specific activity, the specific activity of a reacted fraction, and the fraction reacted are known, when material having low specific activity is used.

Experimental

Benzoic acid, carboxyl- C^{14}

Various techniques for preparing carboxyl-labeled acids by carbonation of the appropriate Grignard reagent with labeled carbon dioxide have appeared in the literature. A summary of most of these appears in "Isotopic Carbon" (3). Carboxyl-labeled benzoic acid has been prepared by Dauben, Reid, and Yankwich (5).

Phenylmagnesium bromide (10 millimoles) was prepared in a 50 ml. round bottomed flask under nitrogen, using a Rosinger magnetic stirrer.* The Grignard was frozen by immersing the flask in liquid nitrogen. The flask was then connected to a high vacuum line and evacuated to 10^{-3} mm. Carbon dioxide was generated in the vacuum system by heating labeled barium

* Essentially a short rod of Alnico steel driven by a rotating magnet. We have found this to be much simpler than the complicated induction stirrer used in high vacuum systems by many workers.

carbonate with eight to ten times its weight of lead chloride to about 350° C. (6). The carbon dioxide was frozen down into the Grignard flask, using liquid nitrogen. The flask was isolated from the vacuum line by closing a stopcock; the mixture was allowed to melt and was vigorously stirred. The freezing, melting, and stirring cycle was repeated. The addition product was then hydrolyzed with dilute sulphuric acid, and the benzoic acid extracted with ether. The acid was extracted from the ether into 1 *N* sodium hydroxide, precipitated with 6 *N* hydrochloric acid, and filtered on sintered glass. Yields were 80 to 85%, based on barium carbonate. Radiochemical yields were not determined.

Ethyl benzoate, carboxyl - C¹⁴

The ester was prepared through the acid chloride. Benzoic acid (10 millimoles) was heated with an excess of thionyl chloride (25 millimoles). When evolution of hydrogen chloride ceased, the excess thionyl chloride was distilled off under slightly reduced pressure, through a small fractionating column. An excess of absolute alcohol (40 millimoles) was added and the mixture refluxed for two hours. The excess alcohol was distilled at atmospheric pressure, then the ester fractionated at reduced pressure.

Alkaline hydrolysis of ethyl benzoate, carboxyl - C¹⁴

Ethyl benzoate (9 millimoles) was hydrolyzed in 100 ml. of a solution 50% by volume alcohol and 0.5 *N* with sodium hydroxide, for a short period. One-half of the solution was then diluted with 200 ml. of water and extracted with ether to remove unhydrolyzed ester. The aqueous solution was acidified and the benzoic acid extracted with ether. The ether layer was washed with water and evaporated under slightly reduced pressure in a stream of nitrogen. The benzoic acid was taken up in 15 ml. of alcohol and divided into two fractions of 5 and 10 ml. respectively. These fractions were titrated with 0.05 *N* sodium hydroxide, using phenol red indicator. Each fraction was then diluted to 25 ml. with water containing 1% of hydrazine hydrate. After hydrolysis was completed in the second half of the main solution, a 6 ml. sample was withdrawn. The benzoic acid was isolated and divided into two fractions in the same way as before. After titration, they were diluted to 25 ml. also. These four sodium benzoate solutions were used for counting.

Samples for volumetric analysis for benzoic acid were taken from the main solution at the end of the short hydrolysis period, and after complete hydrolysis, to determine the fraction of ester hydrolyzed in the initial hydrolysis period.

The radiochemical purity of the benzoate solutions was checked in the following manner. After samples of the benzoate solutions had been counted, each solution was acidified with sulphuric acid and the benzoic acid re-extracted with ether. The ether solutions were washed with water twice and the benzoic acid was isolated and sodium benzoate solutions prepared for counting as before. The specific activities remained constant.

Sample Mounting for Counting

The benzoic acid was counted as sodium benzoate. Samples of 50 λ or 100 λ of the sodium benzoate solutions obtained were pipetted onto stainless steel disks. The disks were 2.5 cm. in diameter, having an area of 3.45 cm.² defined by a thin, 2 mm. wide, ring of Tygon paint primer around the outside rim. The samples were dried under an infrared lamp, with a gentle stream of air directed toward the disk. With hydrazine hydrate present, the solutions spread fairly well, and, with a little care, a uniformly thin layer of salt was obtained. Sample thickness ranged from 0.05 to 0.2 mgm. per cm.², the actual thickness depending on the fraction and sample volume.

Counting

The samples were counted in a Simpson type, methane filled, proportional counter with linear amplifier (National Research Council, Atomic Energy Project, "Methane, low level β -counter assembly, 505A"). In this type of instrument the count recorded is relatively insensitive to changes in area of samples being counted, as long as the thickness of any sample is very small and is reasonably uniform; in other words, as long as self-absorption is negligible. The geometry obtained is slightly greater than 50% because of back-scattering. At the sample thickness used, self-absorption was negligible, since a constant counting rate per milligram of material was obtained when the thickness was varied by a factor of four.

Results

Analytical and counting results are summarized in Table I.

TABLE I
EXPERIMENTAL RESULTS

Material sampled	Time of sampling	Weight of acid, gm.	Specific activity, counts/min./mgm.
Acid produced in initial hydrolysis	5 min.	0.112	$a' = 8,179 \pm 80$
Acid produced by complete hydrolysis	72 hr.	1.11	$a = 9,427 \pm 115$

From these experimental values, $f = 0.101$ and $r = 0.87 \pm 0.016$. Using Equation (3), $k^*/k = 0.86 \pm 0.016$ or $k/k^* = 1.16 \pm 0.017$, where the limits shown represent the errors in internal consistency in sampling and counting.

Conclusion

From these results, and those of others noted in the introduction, it becomes obvious that in the case of C¹⁴ care must be taken in the quantitative interpretation of data obtained in tracer experiments wherever all reactions do not go essentially to completion.

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THE CATALYTIC OXIDATION OF ETHYLENE TO ETHYLENE OXIDE¹

By F. L. W. McKIM AND A. CAMBRON

Abstract

The catalytic oxidation of ethylene to ethylene oxide was investigated in flow experiments over silver catalysts at atmospheric pressure between 260° and 350° C. Calcium oxalate and stannous oxide were used as catalyst promoters. Close temperature control was provided by mounting the catalyst on a silver support. At 270° C. the selectivity increased from about 25%, with ethylene in large excess, to about 55%, with oxygen in large excess. With air constant and in large excess, the over-all reaction rate was found to be proportional to the square root of the ethylene concentration. With ethylene constant and in large excess, the reaction rate was found to be roughly proportional to the oxygen concentration. The presence of methane, ethane, or propane promoted the complete oxidation of ethylene to carbon dioxide and water. In the absence of paraffins the addition of traces of ethylene dichloride only served to poison the catalyst.

Introduction

Ethylene oxide was first prepared by Wurtz (38) in 1859 by the action of alkali on ethylene chlorhydrin. The latter compound, which Wurtz had also been the first to prepare, had been obtained by the action of hydrochloric acid on ethylene glycol. The method used by Wurtz for preparing the oxide is still the most convenient laboratory method and is also one of the commercial methods in use to-day for preparing that chemical, which is becoming increasingly important as a starting material in organic syntheses.

During the past 20 years another and more direct method for obtaining ethylene oxide has been investigated. This method consists in the oxidation of ethylene by elementary oxygen to ethylene oxide. In an investigation of the noncatalytic reaction between ethylene and oxygen, Lenher (21) found ethylene oxide and formaldehyde to be the primary reaction products. Other oxidation products identified by Lenher were dioxymethyl peroxide, acetaldehyde, formic acid, water, and the oxides of carbon. Lenher found that both the rate of reaction and the amounts of the various reaction products were influenced by the nature and extent of the surface of the reaction vessel. He concluded that some steps of the reaction took place at the wall of the vessel. This method for the preparation of ethylene oxide was the subject of a patent assigned to duPont (22). Geib and Harteck (11) reported the formation of ethylene oxide when oxygen atoms reacted with ethylene at -183° C.

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Recently, Newitt and Mene (27) have reported obtaining ethylene glycol by the oxidation of ethylene at pressures between 10 and 100 atm. at 200° C.

Subsequent to Lenher's publication, Francon (10) published the results of an investigation of the catalytic oxidation of ethylene to ethylene oxide. Ethylene oxide, carbon dioxide, and water, together with traces of aldehydes, were the only oxidation products. In this paper Francon described the conditions under which the reaction was carried out but did not disclose the preparation or composition of the catalyst. Francon's method was the subject of several patents assigned to Société Française de Catalyse Généralisée (33) and to Carbide and Carbon Chemicals Corporation (20). Although the first reference to the use of silver as a catalyst in the air oxidation of ethylene was made by Walter (37), the former patents (20, 33), and those assigned to Dreyfus (9) were the first disclosures of the use of silver as a catalyst in the vapor phase oxidation of ethylene to ethylene oxide. Several other metals, such as antimony, lead, copper, and iron, were also claimed to be active as catalysts in this reaction; but in the course of later investigations silver was found to be the only practical catalyst and in the numerous later patents the use of silver has been the subject of specific claims.

Reference to the use of silver as a catalyst for the oxidation of ethylene to ethylene oxide has also appeared in a thesis by A. Hecker (12) and in a paper by Reyerson and Oppenheimer (31), who described experiments in which they compared the activity of silver catalysts prepared by different methods with the activity of a silver catalyst claimed to be in commercial use for the production of ethylene oxide. McBee, Hass, and Wiseman (24) have reported an investigation of the catalytic air oxidation of ethylene using a silver catalyst prepared by coating pieces of corundum with silver oxide.

More recently Twigg (34) has investigated the mechanism of the silver catalyzed oxidation of ethylene by experiments in both flow and static systems. He concluded that the first step in the reaction is adsorption by the catalyst of oxygen in the form of atoms. Ethylene, which was found to be either not adsorbed at all or only weakly adsorbed by Van der Waal's forces, would then react either with one adsorbed oxygen atom to form ethylene oxide or with a pair of atoms to form an intermediate that is rapidly oxidized to carbon dioxide and water. Some of the carbon dioxide and water may also be formed by oxidation of the ethylene oxide via acetaldehyde.

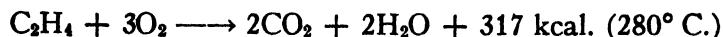
The aim of the present work was the production of an active and stable silver catalyst and the development of a reactor design that would give close temperature control of the catalyst surface. The effect of the presence of methane and ethane on the reaction were also to be investigated.

Choice of Catalyst Support

The formation of ethylene oxide from ethylene and oxygen is a mildly exothermic reaction:



but the complete combustion of ethylene to carbon dioxide and water is strongly exothermic:



It was realized that one of the major problems in controlling reaction conditions was the design of a reactor that would provide a large catalyst area per unit volume but would allow close temperature control at all points of the catalyst surface.

Although Langwell *et al.* (17) have recommended coating the catalyst in a thin layer on a removable metal support in a tube bundle heated by a boiling liquid, all the other workers in this field have used as the catalyst support refractory materials such as fused alumina pellets (5), sandstone, porous artificial silica filter stone (18) and fire brick (26). When glass wool or fused alumina pellets were used as supports for an active silver catalyst in preliminary experiments in Pyrex tubes, it was observed that as the ethylene rate was increased, the entrance end of the catalyst bed would begin to glow, the local rise in temperature resulting in excessive carbon dioxide formation and in sintering and deactivation of the catalyst.

This defect of catalyst supports of low thermal conductivity has been reported by several workers. Hecker (12), using a silver catalyst supported on glass wool, reported a decrease in selectivity* from 48 to 30% as the ethylene concentration was increased from 3 to 13%. McBee *et al.* (24) showed that good temperature control could be obtained with a corundum catalyst support at low ethylene rates. In one series of experiments, however, they reported a decrease in the ethylene oxide produced as the total flow rate was increased. This was very probably caused by increased combustion of the ethylene to carbon dioxide and water resulting from poor temperature control at the higher flow rate.

The laboratory reaction tubes described below, in which silver sheet is used as the catalyst support, were used in an attempt to solve the temperature control problem in laboratory experiments. A description of the "fin reactor", which was felt to be easily adaptable to larger scale experiments, will form the subject of a later communication.

Methods of Preparation of Silver Catalysts

The methods disclosed in the literature for preparing finely divided silver or silver oxide include the following, most of which have been patented as methods for preparing silver catalysts.

1. The thermal decomposition of silver salts of nitrophenols (13), silver oxalate (12, 15, 35), silver cyanide (28), silver carbonate and silver oxide (16).
2. The precipitation of silver oxide by the addition of a solution of sodium hydroxide to aqueous silver nitrate (32).

* The term selectivity is used to denote the per cent yield of ethylene oxide based on ethylene reacted.

3. The reduction of silver nitrate with hydrogen (6).
4. The reduction of silver compounds in an aqueous medium by nascent hydrogen (36).
5. The electrolysis of solutions of potassium nitrate or silver nitrate between silver electrodes (29).
6. The reduction of silver compounds by various reducing agents—e.g., formaldehyde, hydrazine, hydroxylamine (7).
7. Reduction of silver chloride with ferrous citrate (30).

Promoters

In addition to disclosing silver as a catalyst in the catalytic oxidation of ethylene to ethylene oxide, the original Lefort patent (20) disclosed gold, copper, iron, antimony, bismuth, lead, nickel, tin, arsenic, both as catalysts in their own right and as promoters with silver. Van Peski (35) reported gold, copper, and manganese as useful promoters, manganese also being used later by Hecker (12). Carter (5) disclosed that small amounts of compounds of alkali and alkaline earth metals, when used with silver supported on fused aluminum oxide, improved the activity and ruggedness of the catalyst. In a later patent, McNamee and Blair (25) reported that the oxides, hydroxides, and peroxides of barium, strontium, and lithium were the most useful oxides, hydroxides, and peroxides of the alkali and alkaline earth metals. Calcium oxides or hydroxide were also reported to increase the activity of the catalyst but the increased activity was accompanied by excessive carbon dioxide formation. Recently Mawer (26), in contradiction to McNamee and Blair, has reported calcium peroxide as an active promoter for silver in his reaction, and obtained selectivities as high as 64 to 68% without the use of an inhibitor.

Experimental

Preparation of Catalyst

In addition to the method described below, a number of methods of preparing an active silver catalyst were investigated, such as the thermal decomposition of silver oxalate in xylene at 200° C., in aqueous monoethanolamine at 60° C., the reduction of silver sulphite by monoethanolamine at 90° C., the precipitation of silver oxide by sodium hydroxide at 20° C., and the decomposition of silver nitrite at 300° C. The particle size of the silver catalysts prepared by the above methods was determined by the X-ray diffraction method and found to lie between 100 to 150 Å units.

It was found that the activity of unpromoted silver catalysts prepared by precipitation of silver or of silver oxide, or by thermal decomposition of an organic silver salt, was a function of the particle size of the silver, and was independent of the method used in their preparation.

The method used for the preparation of the catalyst in our experiments was the thermal decomposition of silver oxalate in the presence of water in an autoclave, sufficient water being added to maintain a liquid phase during the exothermic decomposition; this prevented local overheating and sintering of

the silver. Rapid decomposition of the oxalate began at about 110° C. and caused the temperature of the charge to rise to about 200° C.

Previous investigators who prepared finely divided silver by the thermal decomposition of the oxalate used dry silver oxalate as starting material (12, 15, 35). We found this procedure unsatisfactory on account of the explosive nature of the dry silver salt. By proceeding as outlined above, the decomposition of the oxalate takes place smoothly and a uniformly fine product is obtained with a particle size, as determined by the Laue-Brill method, of about 130 Å.

Pure silver catalysts prepared by any of the methods mentioned above showed a high initial activity when used at about 300° C., but the activity decreased rapidly owing to sintering. The stability and activity of such catalysts were found to be greatly increased by the addition of small percentages of calcium oxalate and stannous oxide. The calcium oxalate was coprecipitated with the silver oxalate, before decomposition, from a nitrate solution with sodium oxalate. The optimum amount of calcium oxalate has been found to be between 1 and 10% of the finished catalyst. Stannous oxide was added to the mixed silver-calcium oxalates either before or after thermal decomposition of the oxalates. The amount used was 2 to 10% of the silver.

Calcium oxalate and the oxides of tin and cadmium were investigated as promoters for silver because of the proximity of the oxide crystal lattice dimensions to those of silver oxide.

TABLE I
CRYSTAL LATTICE DIMENSIONS (ANGSTROM UNITS)

Substance	System, structure	Lattice constants		
		(a)	(b)	(c)
Ag	Cub., f.c., (Cu)	4.078	—	—
Ag ₂ O	Cub., f.c., (Cu ₂ O)	4.72	—	—
CaO	Cub., f.c., (NaCl)	4.797	—	—
SnO	tetr. (PbO)	3.77	—	4.77
SnO ₂	tetr.	4.72	—	3.16
CdO	Cub., (NaCl)	4.689	—	—

Example

Two hundred grams of silver nitrate and 3.1 gm. of calcium nitrate (Ca(NO₃)₂ · H₂O) were dissolved in 1.5 liters of distilled water. Eighty-four grams of sodium oxalate was dissolved in 1.5 liters of distilled water at 60° C.; this solution was filtered and added with stirring to the silver nitrate solution. The precipitate was allowed to settle, the supernatant solution decanted, and the precipitate stirred three times with 3 liters of distilled water, the precipitate being allowed to settle, and the clear liquid decanted between each washing. The precipitate was then filtered by suction and stored in a dark space.

The thermal decomposition of the mixed oxalates was effected by heating in the presence of water in an autoclave. One hundred and eighty grams of the mixed silver-calcium oxalates was made up into a paste with 160 cc. of water in a silver cylinder that fitted snugly in the autoclave. Before heating the autoclave, the air was swept out with carbon dioxide and after closing the autoclave the temperature was raised to 200° C. The observed pressure at this temperature was 175 kgm. per sq. cm. The heating cycle was approximately 15 min. heating to 200° C., 45 min. cooling to 150° C., at which temperature the pressure was released.

In order to obtain the catalyst in a form suitable for application to the metal support, the product obtained by the thermal decomposition of the silver and calcium oxalates was mixed with glycol in the proportion of 50 gm. of glycol to 100 gm. of catalyst. Finely ground stannous oxide (—325 mesh) was added at this point in the proportion of 2% of the weight of the silver. In order to break up the small aggregates of silver formed during the thermal decomposition of the oxalates, the glycol-catalyst mixture was milled for 15 hr. in a 1 liter Abbé mill with two steel cylinders 1 by $3\frac{1}{2}$ in. By this treatment the catalyst was obtained as a thin paste that could be applied to a metal surface by brushing. The amount of dry catalyst required to coat a metal support in this manner was about 70 gm. per sq. m. A paste of suitable consistency for application to a metal support by dipping or spraying may be obtained by adjusting the proportion of glycol.

The silver nitrate, sodium oxalate, and calcium nitrate used were of "A.R." purity. The stannous oxide labeled "Pure" was obtained from the City Chemical Corporation, New York.

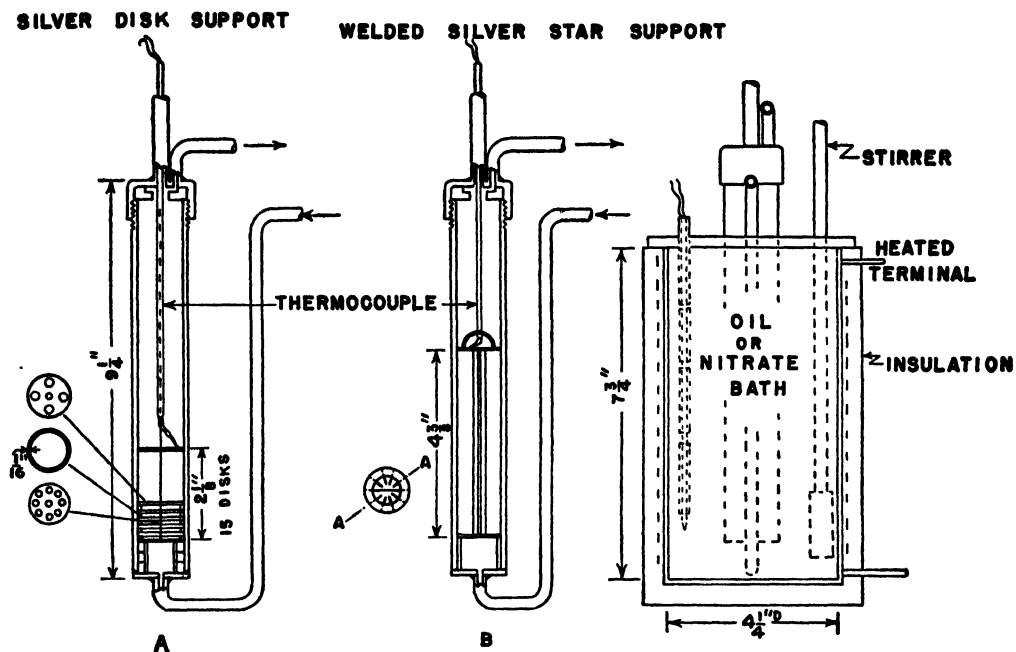
Apparatus and Experimental Procedure

Catalyst Supports and Reaction Tube

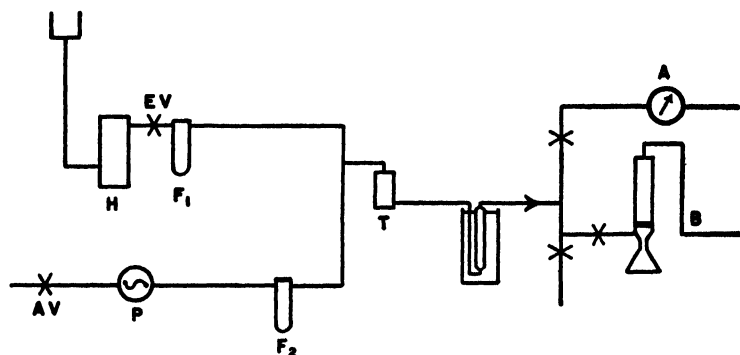
Fig. 1 shows the reaction tube, constant temperature bath, and two types of silver sheet catalyst supports used in our experiments.

The silver disk support, *A*, consisted of 15 disks, 1 by $1/32$ in., coated with catalyst and spaced $1/10$ in. apart by snugly fitting silver rings. Area of disks coated with catalyst, 135 sq. cm.; free space, 20 cc. This design, although providing a larger catalyst area per unit volume than the "star" support described below, had certain defects and was later discarded. Separation of the rings from the disks after repeated heating and cooling was observed with 2-in. disks in a 2 in. tube, and adequate temperature control was difficult with reactors larger than 1 in. diameter. This was due to the poor thermal contact between the disks and the tube wall. Difficulty was also frequently encountered in packing the disks and rings properly in the tube.

Another catalyst support used in laboratory experiments to evaluate catalysts was the "star" welded silver strip support, *B*, shown in Fig. 1. The "star" support used in the experiments reported below was $4\frac{1}{2}$ in. long by 1 in. in diameter and consisted of ten $4\frac{1}{8}$ by $\frac{3}{8}$ by $1/32$ in. silver strips welded

FIG. 1. *Stainless steel reaction tube.*

to silver rings at both ends. The area of the silver strips was 212 sq. cm. and the free space was 55 cc. One and one-half to two grams of a silver catalyst mixed in a smooth paste in glycol was required to coat this support by brushing. The use of a one-piece silver support has a definite advantage over a discontinuous support such as the one described above in that the true temperature of the catalyst can be more accurately measured by one thermocouple brazed to the support.

FIG. 2. *Diagrammatic sketch of apparatus.*

The assembled apparatus is shown diagrammatically in Fig. 2. The ethylene was stored in a 30 liter gas holder, *H*, under a constant 7 ft. head of water. The flow of ethylene was regulated through the valve, *EV*, and measured through the glass capillary flow meter, *F*₁. When other gases, such as methane, ethane, propane, hydrogen, or carbon dioxide were added to the

air-ethylene feed, these gases were stored separately in gas holders similar to *H*, and were metered through individual flow meters. During quantitative tests the ethylene was measured directly from a 1 liter calibrated gas holder. The air supply was measured through the flow meter, *F*₂. It was found advisable to insert in the air line a small tower containing cotton wool and active charcoal to remove any oil spray from the compressor and any other impurities such as hydrogen sulphide that might appear from time to time in the air supply. A tower of indicating "Drierite", *T*, inserted in the gas line after mixing of the air and ethylene was found useful in maintaining a uniformly dry gas mixture. The off-gas rate was measured by a wet test meter, *A*. An absorption tower, *B*, fitted with a 30 mm. sintered glass diaphragm was used in analyzing the off-gas for ethylene oxide and carbon dioxide. Chromel-alumel thermocouples and a Leeds & Northrup potentiometer were used to measure the temperatures of the catalyst support and of the oil bath (Fig. 1). The temperature of the catalyst support was controlled within $\pm 2^\circ \text{C}$. by the use of either a Hoskins RM type temperature controller or a Foxboro potentiometer type controller.

Ethylene Purity

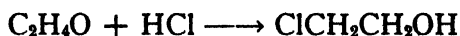
The ethylene obtained in cylinders from the Ohio Chemical Company was derived from alcohol and was "99.5% USP". Samples from two cylinders analyzed at the U.S. Bureau of Standards with the mass spectrometer were both found to contain the following impurities: air, butene-2, *n*-pentane, and diethyl ether. Methane and ethane supplied from the same source were claimed by the manufacturer to be of 90% and 95% purity respectively and were not analyzed. The propane used was a commercial grade of approximately 98% purity.

Analytical Methods

In the experiments reported, ethylene oxide, carbon dioxide, and water were the only products of the reaction.

The ethylene content of the hydrocarbon-air mixture used, and of the product, was determined in our early work by absorption in fuming sulphuric acid in an Orsat type gas analysis apparatus, using mercury as confining liquid. More recently a sodium nitrate-mercuric nitrate-nitric acid solution (8) has been found to be a more convenient reagent.

Ethylene oxide was determined by scrubbing the off-gas (or a measured fraction thereof) at a rate not exceeding 120 liters per hour for 5 to 10 min. through the absorption tower, *B* (Fig. 2), containing 20 to 50 cc. of 0.1 to 0.6 *N* hydrochloric acid saturated with magnesium chloride. Ethylene oxide reacts quantitatively with such a solution to form ethylene chlorhydrin (14, 23):



and was determined by titration of the residual free acid with 0.1 to 0.4 *N* sodium hydroxide solution, using methyl orange-indigo carmine indicator. The accuracy of this method for determining ethylene oxide in the off-gas

was confirmed by scrubbing the off-gas through dilute sulphuric (0.5 to 2%) at 70° C. Under these conditions ethylene oxide is quantitatively converted to mono- and diethylene glycol. After neutralization of the sulphuric acid the glycols were recovered by fractionation.

A rough estimate of the amount of ethylene oxide in the off-gas could be rapidly and conveniently made by bubbling the off-gas through 2 cc. of the hydrochloric acid-magnesium chloride reagent (containing one drop of the methyl orange-indigo carmine indicator) in a test tube and noting the time taken for the indicator to change color.

The carbon dioxide in the off-gas was determined by an absorption method similar to that used for the ethylene oxide determination. The off-gas (or a measured fraction thereof) was scrubbed at a rate not exceeding about 120 liters per hour for three to five minutes through 100 cc. of 0.1 to 0.4 *N* sodium hydroxide solution, and the carbon dioxide was determined by addition of excess barium chloride and titration of the residual caustic with 0.1 to 0.6 *N* hydrochloric acid, using phenolphthalein as indicator. This is a modification of the method described by W. B. Brown (4).

Results

Effect of Temperature on the Promoted and on the Unpromoted Catalyst

The effect of temperature on the per cent conversion of ethylene to ethylene oxide per pass, and on the selectivity, is shown in Fig. 3 and Table II for pure silver, silver + 1.3% calcium oxalate, and silver + 1.3% calcium oxalate + 2% stannous oxide over the range 260-350° C.

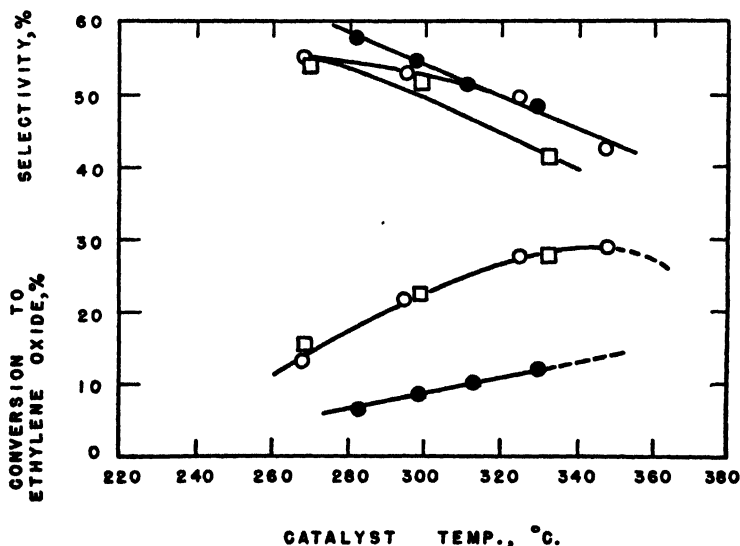


FIG. 3.—Effect of temperature on conversion and selectivity.

● pure silver, ○ silver + 1.3% calcium oxalate,
□ silver + 1.3% calcium oxalate + 2% stannous oxide.

TABLE II

EFFECT OF TEMPERATURE ON CONVERSION AND ON SELECTIVITY

One-inch stainless steel reaction tube; "star" silver support. Area = 106 cm.²; ethylene 5.4 liters per hr.; air, 81 liters per hr. (22° C., 760 mm.); time of contact (300° C.) = 1.3 sec. Tests made after catalyst had been conditioned for 24 hr. at 300° C.

Catalyst	Catalyst temperature, °C.	Conversion of ethylene to ethylene oxide, %	Selectivity, %
Pure silver	282	7.6	58.0
	298	9.2	55.0
	312	10.8	51.0
	329	12.7	48.5
Silver + 1.3% calcium oxalate	268	14.1	55.5
	295	21.9	53.0
	325	27.9	49.5
	348	29.1	42.5
Silver + 1.3% calcium oxalate + 2% stannous oxide	268	16.0	55.0
	298	23.1	51.5
	332	28.1	41.0

As shown in Fig. 3, the promoted catalysts gave much higher conversions, accompanied by somewhat lower selectivity, than the pure silver. The addition of 2% stannous oxide to the silver-calcium oxalate catalyst had no appreciable effect on the per cent conversion of ethylene to ethylene oxide per pass. Whereas the pure silver catalyst showed appreciable signs of sintering after 24 hr. at 300° C., catalysts promoted with calcium oxalate and stannous oxide have been used continuously for six weeks at that temperature without any decrease in activity or any sintering visible under the microscope.

Effect of Air Ethylene Ratio and of Time of Contact

The results of Expts. 1 to 9, as listed in Table III and plotted in Fig. 4, show the effect of varying the air-ethylene ratio on the conversion of ethylene to ethylene oxide and on the selectivity. These single-pass experiments were made with the 1 in. stainless steel reaction tube containing 15 silver disks coated with a silver catalyst containing 1.3% calcium oxalate and 2% stannous oxide. The catalyst temperature was 302° C.

At the three ethylene rates used, beginning with an air-ethylene ratio of 5/1 or less, increasing the air-ethylene ratio by increasing the air rate (and total flow rate) caused an initial increase in both selectivity and conversion. After an air-ethylene ratio of about 10/1 was reached in each case, doubling the air-ethylene ratio (and approximately halving the time of contact) by doubling the air flow rate had almost no effect on the conversion or selectivity.

Fig. 4 shows that for the same air-ethylene ratio a slight improvement in selectivity was observed as the time of contact was decreased, this effect of time of contact on selectivity being less pronounced at low air-ethylene

TABLE III

EFFECT OF VARYING AIR-ETHYLENE RATIO AND TIME OF CONTACT ON CONVERSION TO ETHYLENE OXIDE AND ON SELECTIVITY

Run No.	Ethylene input, liters/hr.*	Air input, liters/hr.*	Air-ethylene	Time of contact, sec.**	Conversion of ethylene to ethylene oxide, %	Total ethylene reacted, %	Selectivity %
1	2.8	13	4.6	2.1	25.0	53.0	47.5
2	2.8	25	8.9	1.2	32.5	66.0	49.5
3	2.8	52	18.5	0.6	34.5	68.5	50.5
4	5.6	25	4.5	1.1	22.5	46.5	48.5
5	5.6	52	9.3	0.6	25.5	49.0	52.0
6	5.6	104	18.5	0.3	25.5	48.0	53.0
7	12.0	25	2.1	0.9	9.2	21.7	42.5
8	12.0	52	4.3	0.5	15.0	31.0	48.5
9	12.0	104	8.7	0.3	17.5	34.0	51.0
10	8.4	78	9.3	0.4	21.0	43.0	50.5

* At 22° C., 760 mm.

** At 302° C.

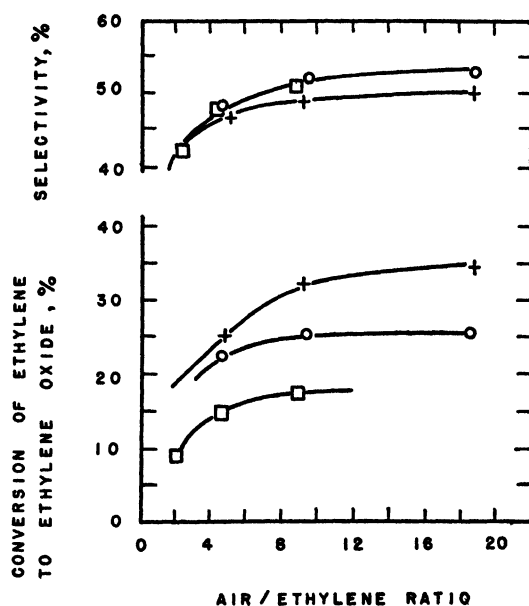


FIG. 4. Effect of varying the air-ethylene ratio.

+ 2.8 liters/hr. ethylene,

O 5.6 liters/hr. ethylene,

□ 12.0 liters/hr. ethylene.

ratios. In Fig. 5, log total liters per hr. of ethylene reacted is plotted against log average ethylene rate for all runs where the air-ethylene ratio was greater than 5/1. The slope of the straight line through the points is 0.48; this indicates that the total reaction rate was approximately proportional to the square root of the average ethylene flow rate. It follows, therefore, that at a

constant air rate when air is in large excess the rate of reaction is proportional to the square root of the ethylene concentration.

This relation between the reaction rate and the ethylene concentration is similar to the relation observed by Benton and Elgin (2) and Benton (1) between the reaction rate and hydrogen concentration in their investigation

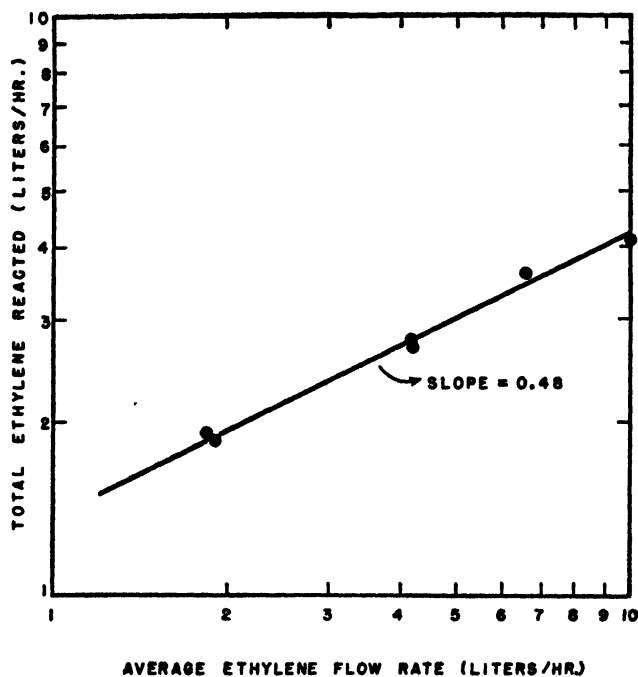


FIG. 5. Relation between total reaction rate and average ethylene flow rate.

of the combination of hydrogen and oxygen over silver. Thus, the oxidation of ethylene on silver would appear to be another example of the special case discussed in the latter paper, involving two reacting gases one of which is strongly adsorbed, the reaction product being also strongly adsorbed and reaction rate being proportional to the square root of the concentration of the gas that is not adsorbed.

Ethylene in Excess

The experiments reported in Table IV were made with the 1 in. stainless steel reaction tube and the "star" silver support (Fig. 1). Two grams of catalyst (silver + 1.3% calcium oxalate + 2% stannous oxide) was used and the catalyst temperature throughout the runs was 270° C. It will be noted that the selectivities are low and decrease with decreasing oxygen-ethylene ratio—in agreement with predictions based on the earlier results reported in Table III. In the runs with ethylene in excess, the rate of reaction was approximately proportional to the oxygen concentration. Nitrogen dilution at a 4/1 nitrogen-oxygen ratio had little effect on the rate of reaction or selectivity. For comparison the selectivity obtained in a run at 268° C.

TABLE IV
ETHYLENE IN EXCESS

Ethylene, liters/hr.*	Nitrogen, liters/hr.*	Oxygen, liters/hr.	Oxygen/ ethylene	Time of contact, sec.	Total ethylene reacted, %	Selectivity, %
50	20	5.2	0.104	1.3	3.6	34
50	—	4.9	0.098	1.8	3.8	33.5
50	—	2.23	0.045	1.9	1.8	25
5.0	59	15.7	3.1	1.3	29	55**

* 0° C., 760 mm.

** Air in excess; these figures were taken from Table II for comparison.

with oxygen in excess has been taken from Table II and entered at the bottom of Table IV. It will be noted that the selectivity increases from about 25% of the total ethylene reacted with ethylene in large excess to about 55% with oxygen in large excess.

Effect of Paraffins and Propane

It has been observed that the addition of methane and ethane and, to a more marked degree, propane to the ethylene-air mixture caused a depression in the rate of conversion of ethylene to ethylene oxide, an effect that persisted after the addition of the paraffin was stopped. In fact, it took several days of continuous operation with pure ethylene before the initial conversion rate was re-established. Simultaneously with the decrease in per cent conversion to ethylene oxide, the apparent rate of conversion of ethylene to carbon dioxide and water, as indicated by the selectivity, showed a marked increase. The results of several experiments are given in Table V and plotted in Fig. 6.

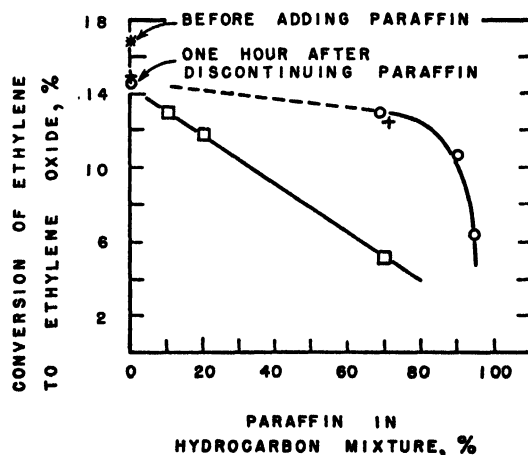


FIG. 6. *Effect of methane, ethane, and propane.*
+ methane-ethylene, ○ ethane-ethylene,
□ propane-ethylene.

TABLE V

EFFECT OF METHANE, ETHANE, AND PROPANE IN THE ETHYLENE FEED ON
CONVERSION TO ETHYLENE OXIDE AND ON SELECTIVITY

One-inch stainless steel reaction tube; 15 silver disks; area, 135 cm.²; 277° C.; 1 atm.; catalyst,
silver + 1.3% calcium oxalate + 2% stannous oxide; air/ethylene, 10-19.

Expt. No.	Ethylene + paraffin, liters/hr.*	Ethylene, liters/hr.*	% paraffin in hydrocarbon gas	Air, liters/hr.*	Conversion of ethylene to ethylene oxide, %	Selectivity,** %
Before adding paraffins						
1	5.4	5.4	0	52	17.0	57.5
Ethylene-methane						
2	18.3	5.3	71	52	12.6	29.5
3	5.4	5.4	0	52	14.7†	34†
Ethylene-ethane						
4	102	5.5	95	52	6.2	15
5	50	5.2	90	104	10.5	25
6	18.2	5.5	70	52	12.9	32
7	5.3	5.3	0	52	14.5†	34†
Ethylene-propane						
8	18.5	5.5	70	104	5.1	—
9	6.8	5.4	20	52	11.8	—
10	6.0	5.4	10	52	13.1	—

* 22° C., 1 atm.

** Uncorrected for paraffin oxidation.

† One hour after discontinuing paraffin.

The above effect has been observed both with the unpromoted and the promoted catalyst.

Effect of Ethylene Dichloride

In experiments with 99.5% ethylene the addition of ethylene dichloride was tried in an attempt to improve the selectivity of the catalyst. It was found, however, that when the dichloride was added in amounts as low as 0.0001% of the inlet gas volume, the catalyst was rapidly poisoned. It was interesting to note that the activity of a catalyst, after it had been poisoned almost completely by this method, could be largely and rapidly restored by the addition of a controlled amount of methane or ethane in the inlet feed gas.

Our experiments suggest that the beneficial effect claimed by Berl (3) and by Law and Chitwood (19) is dependent on the presence of paraffins in the ethylene-air mixture.

Acknowledgment

The assistance of W. A. Tidridge in repeating some of the original work on the effect of temperature on catalyst activity and on the effect of using a high ethylene-air ratio is gratefully acknowledged by the authors.

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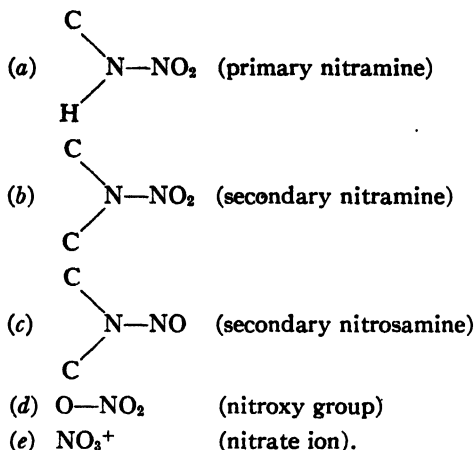
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THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC NITRAMINES, NITROSAMINES, AND NITRATES¹

BY R. NORMAN JONES AND G. DENIS THORN

Abstract

The ultraviolet absorption bands associated with the following groups have been investigated in a variety of compounds of known structure:



The groups may be characterized by the ultraviolet spectrum, and the number of each type of group present in a given compound may be estimated from an analysis of the shape and intensity of the absorption spectrum. These correlations have been applied to the elucidation of the structure of new compounds isolated in the course of the investigation of the chemistry of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).

I. Introduction

In this paper the ultraviolet absorption spectra of some 60 aliphatic nitrogen compounds are recorded. These measurements were made as part of a co-operative investigation of the chemistry of the explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (VII). Many of the compounds examined are intermediates and by-products that were obtained at the University of Toronto and at McGill University during the course of studies on the mechanism of formation of RDX by the Bachmann process. The structures of some of the substances are based on indirect evidence only, and the spectra provided a link in the chain of evidence leading to the structural formulas finally accepted.

In connection with this work, Dr. A. Blomquist kindly made available to us a considerable number of nitramines and derivatives which had been

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prepared at Cornell University by unequivocal methods of synthesis, (4) and these compounds were of great value in establishing empirical relations between structure and spectra. Other compounds were supplied also by Dr. C. B. Purves of McGill University, Dr. W. E. Bachmann of the University of Michigan, Dean F. C. Whitmore and Dr. C. I. Noll of Pennsylvania State College, and Dr. M. Carmack of the University of Pennsylvania.

The spectrographic literature contains only meager references to aliphatic nitrogen containing compounds. Baly and Desch (2), and Hedley (18) in 1908 described the spectra of a few such compounds. Hantzsch and Hein (14) reported on the spectra of several nitro compounds and their alkali salts in 1919 and, more recently, Kortüm has discussed the spectra of several aliphatic nitrogen containing compounds (20-22) including a few simple nitramines (22).

In Table I, references are listed to the published work on the spectra of nitramines, nitrosamines, nitrosohydroxylamines, nitrate and nitrite esters, nitroxy, and nitroso compounds of interest in connection with the chemistry of explosives.

TABLE I

REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS

Formula	Compound	Alternative names and symbolic designations	References*
H ₂ N ₂ O ₂ H ₂ N ₂ O ₃ H ₄ N ₂ O ₃	Nitramide Nitrohydroxylamine Ammonium nitrate	Nitramine	2, 22, * 22 19
CN ₄ O ₈ CHN ₃ O ₆ CH ₂ NO ₂ Br CH ₂ N ₂ O ₄ CH ₃ NO ₂ CH ₃ NO ₂ CH ₃ N ₃ O ₃ CH ₃ N ₂ O ₂ CH ₄ N ₂ O ₂ CH ₄ N ₂ O ₂ CH ₄ N ₂ O ₄ CH ₄ N ₂ O ₄ CH ₄ N ₂ O ₄	Tetranitromethane Trinitromethane Bromonitromethane Dinitromethane Mononitromethane Methyl nitrite Mononitrourea N-Methylnitrosohydroxylamine Methylnitramine Nitroguanidine Methylenedinitramine Methylene-bis-nitrosohydroxylamine	Nitrocarbamide Picrite "Traube Compound"	16, 21 14, 21 18 14, 18, 21 2, 10 26 2 22 2, 6, 9, 22 2, 8 6, * 9, *
C ₂ H ₅ NO ₂ C ₂ H ₅ NO ₃ C ₃ H ₅ N ₂ O ₃ C ₃ H ₅ N ₂ O ₃	Nitrosoethane Nitroxyethane 1-Nitroxy-2-nitro-2-azapropane 1-Nitroxy-3-nitro-3-azapropane	Ethyl nitrite Ethyl nitrate 2-Nitroxy ethylnitramine NENA	10, 16, 26 10, 11, 17, 26, * * *
C ₂ H ₅ N ₂ O C ₂ H ₅ N ₂ O ₂ C ₂ H ₅ N ₂ O ₂ C ₂ H ₅ N ₂ O ₄	Dimethylnitrosamine Dimethylnitramine Ethylnitramine Ethylenedinitramine	 EDNA	2, 5, 9, * 9, 22 22 6, 8

* The numerical references relate to the publications listed in the bibliography on page 860. The symbol * in this column indicates that the spectrum of the compound is described in this article.

The preparation and chemical properties of certain of the compounds included in this table have not yet been described fully in the literature (see Introduction, page 828).

TABLE I—*Continued*REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Continued*

Formula	Compound	Alternative names and symbolic designations	References *
$C_2H_{10}N_4O_6$	Ethylenediamine dinitrate		*
$C_5H_4N_4O_5$	2,5-Dinitro-2,5-diazacyclopentanone-1	Dinitroethyleneurea	*
$C_5H_6N_2O_3$	Nitrosourethane		2
$C_5H_6N_2O_4$	Nitrourethane		2, *
$C_5H_6N_4O_5$	1-Oxa-3,5-dinitro-3,5-diazacyclohexane	Cyclonite oxide	*
$C_5H_6N_6O_5$	1,3,5-Trinitroso-1,3,5-triazacyclohexane	Trinitrosotrimethylene-triamine	9, *
$C_5H_6N_6O_5$	1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane	NOX	9, *
$C_5H_6N_6O_5$	1,3,5-Trinitro-1,3,5-triazacyclohexane	Trinitrotrimethylene-triamine. RDX	8, 9, 24, *
$C_5H_7N_2O_3$	1-Nitroso-3-nitro-3-azabutane		*
$C_5H_7N_2O_7$	1,5-Dinitro-3-nitroso-1,5-diazapentane		*
$C_5H_8N_4O_4$	1,5-Dinitro-1,5-diazapentane	1,3-Propylenedinitramine	6
$C_5H_8N_4O_4$	1,4-Dinitro-1,4-diazapentane		*
$C_5H_8N_4O_4$	1,4-Dinitro-2-methyl-1,4-diazabutane		*
$C_5H_8N_4O_4$	Methylene-bis-nitrosohydroxylamine α -methyl ester	Traube Compound α -methyl ester	9, *
$C_5H_8N_4O_4$	Methylene-bis-nitrosohydroxylamine β -methyl ester	Traube Compound β -methyl ester	9, *
$C_5H_8N_6O_7$	1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate	PCX	*
$C_6H_8N_2O_3$	1-Oxa-4-nitro-4-azacyclohexane	N-Nitromorpholine	*
$C_6H_8N_4O_3$	1-Nitro-4-nitroso-1,4-diazacyclohexane	N-Nitro-N'-nitrosopiperazine	*
$C_6H_8N_4O_4$	1,4-Dinitro-1,4-diazacyclohexane	N,N'-Dinitropiperazine	*
$C_6H_8N_4O_5$	1,5-Dinitroso-3-nitro-3-azapentane	DINA	*
$C_6H_8N_6O_5$	1,3,5-Trinitro-1,3,5-triazacycloheptane	Hept.-RDX	*
$C_6H_8N_6O_5Cl_2$	1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane	GSX	*
$C_6H_8N_8O_7$	1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	N-HMX	*
$C_6H_8N_8O_8$	1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane	HMX	9, *
C_6H_9NO	<i>tert</i> -Nitrosobutane		2
$C_6H_8N_6O_5$	1,3-Dinitro-5-methylol-1,3,5-triazacyclohexane		9
$C_6H_8N_6O_5Cl$	1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane	OFX	*
$C_6H_{10}N_2O$	Diethylnitrosamine		2
$C_6H_{10}N_2O_2$	<i>n</i> -Butylnitramine		*
$C_6H_{10}N_2O_3$	N-(Trimethylolmethyl)-nitrosohydroxylamine		6
$C_6H_{10}N_2O_3$	N-(Trimethylolmethyl)-nitramine		6
$C_6H_{10}N_4O_4$	2,5-Dinitro-2,5-diazaheptane	N,N'-Dimethyl EDNA	*
$C_6H_{10}N_4O_5$	1,5-Dinitroso-3-azapentane nitrate		*

TABLE I—*Continued*REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Continued*

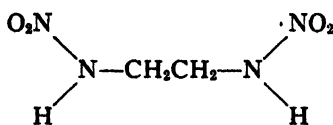
Formula	Compound	Alternative names and symbolic designations	References *
$C_4H_{11}N_6O_4$ $C_4H_{13}N_6O_5$	1,7-Dinitro-1,4,7-triazaheptane 1-Nitroso-3,6-diazaheptane dinitrate		* *
$C_8H_4N_2O_8$ $C_8H_8N_4O_{13}$ $C_8H_8NO_2$	Furfural nitramide Pentaerythratol tetranitrate 2-Methyl-2-nitrosobutanone-3	PETN <i>tert</i> -Nitrosoisopropyl-acetone TAX	* 24 2, 13
$C_8H_9N_6O_5$	1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane		*
$C_8H_{10}N_6O_2$	Dinitrosopentamethylenetetramine		*
$C_8H_{10}N_6O_4$ $C_8H_{10}N_{10}O_{14}$	Dinitropentamethylenetetramine 1,9-Dinitroso-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	DPT "106"	8, * *
$C_8H_{11}NO_2$ $C_8H_{11}N_6O_4$	<i>n</i> -Amyl nitrite 1,5-Dinitro-3-methyl-1,3,5-triazacycloheptane		2, 5, 9 *
$C_8H_{11}N_6O_7$	2,5-Dinitro-7-nitroso-2,5-diazaheptane		*
$C_8H_{12}N_6O_6$	1,5-Dinitro-3-methyl-3-(methylenenitramine)-1,5-diazapentane	PGX	*
$C_8H_{12}N_6O_7$	1-Methoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methoxy-MSX	*
$C_8H_{13}N_6O_4$	2,6-Dinitro-4-methyl-2,4,6-triazaheptane		*
$C_8H_{11}N_7O_7$	1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	SEX (QDX)	*
$C_8H_{12}N_6O_8$	1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane	MSX	*
$C_8H_{12}N_6O_{10}$	1,8-Dinitroso-3,6-dinitro-3,6-diazaoctane		*
$C_8H_{13}N_6O_3$	Hexamethylenetetramine mononitrate		*
$C_8H_{14}N_2O_2$ $C_8H_{14}N_4O_9$	Cyclohexylamine nitrite 2,6-Dinitroso-4-azaheptane nitrate		9 *
$C_8H_{14}N_6O_6$	Hexamethylenetetramine dinitrate		*
$C_8H_{14}N_6O_7$	1-Ethoxy-2,4,6-trinitro-2,4,6-triazaheptane	Ethoxy-MSX	*
$C_8H_{16}N_6O_{12}$	1,8-Dinitroso-3,6-diazaoctane dinitrate		*
$C_8H_{18}N_6O_4Cl_2$	1,10-Dinitro-1,4,7,10-tetrazadecane 4,7-dihydrochloride		*
$C_8H_{18}N_8O_{10}$	1,10-Dinitro-1,4,7,10-tetrazadecane 4,7-dinitrate		*
$C_7H_{13}NO_3$ $C_7H_{16}N_6O_6$	α -Methyl-D-glucose-6-nitrate 1,7-Dinitro-4-carboethoxy-1,4,7-triazaheptane		* *
$C_8H_{14}N_4O_8$	1,4-Dicarboethoxy-1,4-dinitro-1,4-diazabutane	Ethylene- <i>bis</i> -nitrourethane	*

TABLE I—*Concluded*REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Concluded*

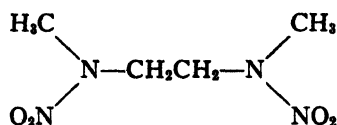
Formula	Compound	Alternative names and symbolic designations	References *
$C_8H_{14}N_6O_{10}$	1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	BSX	*
$C_8H_{17}NO_2$	2-Nitrooctane		25
$C_8H_{17}NO_2$	2-Octyl nitrite		23
$C_8H_{18}N_8O_8$	$\Delta^{4,6}$ -2,10,13-Trinitro-6-oxo-7-oxa-2,5,6,10,13-pentazatetradecane		*
$C_8H_{20}N_4O_2$	Tetraethylammonium nitrate		12, 20
$C_9H_{16}N_8O_{12}$	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	AcAN	*
$C_9H_{18}N_6O_4$	N-Acetylaminomethylhexamethylenetetramine mononitrate	H ₂	*
$C_9H_{18}N_{10}O_8$	Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane		*
$C_{10}H_{19}NO_2$	2,3,4-Trimethyl- β -methyl-D-glucose-6-nitrate		*
$C_{11}H_{19}N_7O_{11}$	1,9-Diacetoxy-2,4,8-trinitro-6-acetyl-2,4,6,8-tetrazanonane	H ₁₆	*
$C_{12}H_{24}N_6O_8$	1,10-Dinitro-4,7-dicarboethoxy-1,4,7,10-tetrazadecane		*
$C_{12}H_{24}N_8O_8$	Tetrapropylammonium nitrate		12
$C_{13}H_{19}NO_{11}$	2,3,4-Triacetyl- α -methyl-D-glucose-6-nitrate		*
$C_{13}H_{19}NO_{11}$	3,4,6-Triacetyl- β -methyl-D-glucose-2-nitrate		*

II. The Spectra of Nitramines

The spectra of aqueous, alcoholic, or dioxane solutions of both primary and secondary nitramines are relatively simple. One broad structureless band is present, with a maximum in the region between 2250 and 2400 Å. The spectrum of a typical primary nitramine, ethylenedinitramine (I), is given in Fig. 1 and that of a typical secondary nitramine, 2, 5-dinitro-2,5-diazahexane (II)*, in Fig. 2.



I



II

* The nomenclature adopted in this article has not been rigidly systematized. For the simpler compounds, the names in common use have been employed, i.e., "methylnitramine". For compounds of more complex structure the systematic "aza" nomenclature has been employed. As applied to heterocyclic compounds, this is described by Patterson, (J. Am. Chem. Soc. 55:3905, 1933); its extension to linear compounds follows logically. In the interests of brevity we have occasionally retained certain of the abbreviations (RDX, DPT, etc.) favored by explosives chemists, where it seemed advantageous to do so; these trivial names and symbolic designations are cross-referenced with the systematic names in Table I.

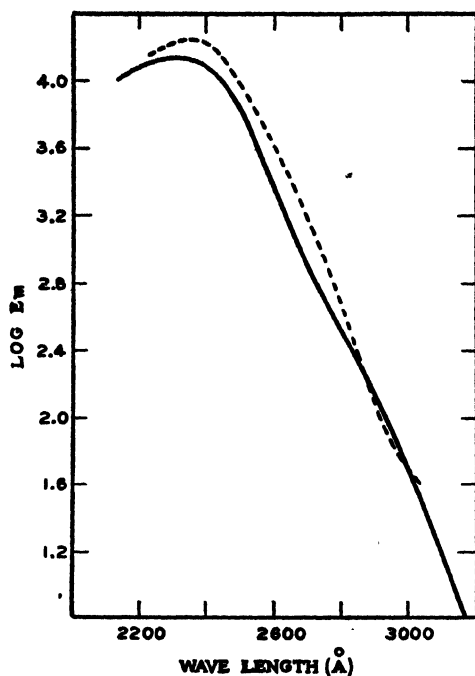


FIG. 1. Spectrum of typical primary nitramine (Ethylenedinitramine).

————— Curve A. Solvent, ethanol.
----- Curve B. " 0.2 N sodium hydroxide.

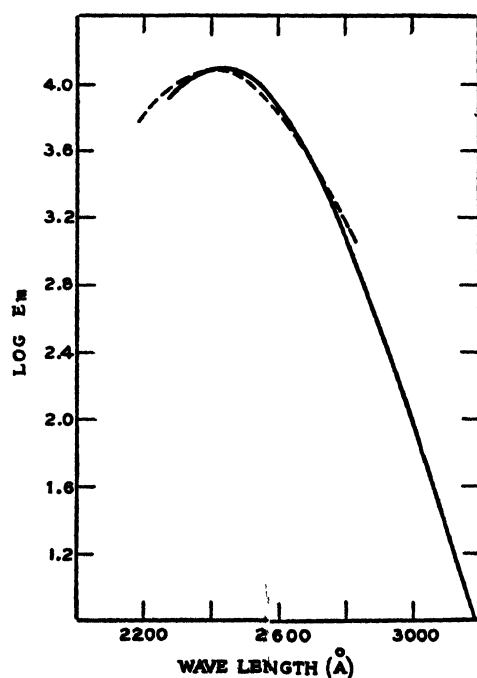


FIG. 2. Spectrum of typical secondary nitramine (2,5-dinitro-2,5-diazahexane).

————— Curve A. Solvent, dioxane.
----- Curve B. " 0.2 N sodium hydroxide.

A. Secondary Nitramines

The wave lengths and intensities of the absorption maxima of a number of secondary nitramines are listed in Table II. For compounds containing one nitramine group per molecule the molecular extinction coefficient at the maximum (E_{\max}) is close to 5500. It is observed empirically that in the

TABLE II
ABSORPTION SPECTRA OF SECONDARY NITRAMINES
WAVE LENGTH AND INTENSITY OF THE MAXIMUM

Structure	Compound	Solvent	Absorption Max.		$\frac{E_{\max}}{5500}$
			λ , Å	E_{\max}	
XL	N-nitromorpholine	Ethanol	2470	5400	0.98
	Dimethylnitramine	Dioxane	2400	6300	1.14
	1,5-Dinitroxy-3-nitro-3-azapentane	Ethanol	2350	6770	1.23*
		Dioxane	2330	7330	1.34
XXXVIII	1-Nitroxy-2-nitro-2-azapropane	Ethanol	2380	6710	1.22*
XIV	Dinitropentamethylenetetramine	Dioxane	2410	11000	2.00
	Dinitropiperazine	Dioxane	2500	11000	2.00
XVIII	1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate	Dioxane	2350	11320	2.06
XVI	1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane	Ethanol	2240	6230	1.13†
		Dioxane	2240	6450	1.17
IX	3,5-Dinitro-1-oxa-3,5-diazacyclohexane	Ethanol	No maximum		
	Dinitroethyleneurea	Ethanol	2460	10500	1.91
II	2,5-Dinitro-2,5-diazaheptane	Dioxane	2410	12250	2.21
XXXVII	2,5-Dinitro-7-nitroxy-2,5-diazaheptane	Dioxane	2410	11850	2.15*
XXXIX	1,8-Dinitroxy-3,6-dinitro-3,6-diazaoctane	Dioxane	2390	12200	2.22*
XXVI	1,4-Dicarboethoxy-1,4-dinitro-1,4-diazaheptane	Dioxane	2350	10250	1.86
	2,6-Dinitro-4-methyl-2,4,6-triazaheptane	Ethanol	2290	13570	2.44
	1,5-Dinitro-3-methyl-1,3,5-triazacycloheptane	Ethanol	2325	13000	2.35
	1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	Ethanol	2280	17000	3.09
XVII	1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	Ethanol	2280	17800	3.24

* The high value for $E_{\max}/5500$ in these compounds is probably associated with the presence of the nitroxy group and is discussed on page 856.

† See discussion on page 843.

TABLE II—*Concluded*
 ABSORPTION SPECTRA OF SECONDARY NITRAMINES
 WAVE LENGTH AND INTENSITY OF THE MAXIMUM—*Concluded*

Structure	Compound	Solvent	Absorption Max.		$\frac{E_{\max}}{5500}$
			λ , Å	E_{\max}	
VII	1-Methoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2350	16200	2.95
	1-Ethoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2350	16600	3.02
	1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2320	16600	3.02
	1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane	Dioxane	2330	17400	3.16
	1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane	Dioxane	2310	18200	3.30
	1,3,5-Trinitro-1,3,5-triazacyclohexane	Ethanol	No maximum		
	1,3,5-Trinitro-1,3,5-triazacycloheptane	Ethanol	2330	14900	2.72
	$\Delta^{5,6}$ -2,10,13-trinitro-6-oxo-7-oxa-2,5,6,10,13-pentazatetradecene	Dioxane	2410	20100	3.66
	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	Dioxane	2320	21900	3.98
	1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	Dioxane	2280	21850	3.97
VIII	1,3,5,7-Tetranitro-1,3,5,7-tetraza-cyclooctane	Ethanol	2280	21400	3.90
	Methylene-bis-3,6-dinitro-1,3,6-triazacycloheptane	Ethanol	2340	23400	4.25

absence of secondary complicating factors E_{\max} increases in direct proportion to the number of nitramine groups in the molecule, so that for a substance containing n secondary nitramine groups the molecular extinction coefficient at the maximum is close to $5500 \times n$. This is illustrated in Column 6 of Table II in which E_{\max} is divided by 5500. We propose to call this factor the *molecular extinction constant* of the secondary nitramine group**.

** Linear relations of this kind, correlating the molecular extinction coefficient at a maximum with the frequency of occurrence of a certain chromophore in a molecule, have not previously been established for any extensive series of compounds and the term molecular extinction constant has not hitherto been used in spectrographic literature. In the general case it may be defined in the following terms. If, in a series of compounds, each of which contains n identical chromophoric groups, the molecular extinction coefficient at the wave length λ (E_λ) can be represented by the equation

$$E_\lambda = nC_\lambda$$

C_λ is the molecular extinction constant of the chromophoric group for the wave length λ .

B. Primary Nitramines

In Table III the absorption data are given for a number of primary nitramines in water, alcohol, or dioxane. Here also a linear relation between the intensity of E_{\max} and the number of nitramine groups in the molecule is observed. The molecular extinction constant for the primary nitramine group at the maximum in neutral solution is 7000. One compound has been examined which contains both a primary and a secondary nitramine group, and in this case (III) the observed extinction coefficient agrees well with that calculated by summation of the molecular extinction constants for one primary

TABLE III
ABSORPTION SPECTRA OF PRIMARY NITRAMINES
WAVE LENGTH AND INTENSITY OF THE MAXIMUM

Structure	Compound	Solvent	Absorption max.		$\frac{E_{\max}}{7000}$
			$\lambda, \text{\AA}$	E_{\max}	
XXII	Nitramide	Water	2250	5900	0.84
	Methylnitramine	$5 \times 10^{-3} N$ HCl	2325	7200	1.03*
	N-(trimethylolmethyl)-nitramine	Water	2350	6970	1.00†
	<i>n</i> -Butylnitramine	Ethanol	2325	7200	1.03
VI	2-Nitroxyethylnitramine	Ethanol	2240	5500	0.80
I	Ethylenedinitramine	Ethanol	2300	13400	1.92
XIX	1,7-Dinitro-1,4,7-triazaheptane	0.2 <i>N</i> HCl	2280	13970	2.00
	Methylenedinitramine	Ethanol	2260	12530	1.80
IV	1,10-Dinitro-4,7-dicarboethoxy-1,4,7,10-tetrazadecane	Dioxane	2350	11500	1.65‡
V	1,7-Dinitro-4-carboethoxy-1,4,7-triazaheptane	Dioxane	2340	11200	1.60‡
XLII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dinitrate	Water	Inflection only		
XLIII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dihydrochloride	Water	2300	15970	2.28
	1,4-Dinitro-2-methyl-1,4-diazabutane	Ethanol	2350	13400	1.92
	1,5-Dinitro-3-nitroxy-1,5-diazapentane	Dioxane	2275	14450	2.06
	1,5-Dinitro-3-methyl-3-(methylenenitramine)-1,5-diazapentane	Ethanol	2350	23800	3.39

* Data taken from measurements of Kortüm (21).

† Data privately communicated by Dr. Carmack (See also references (6, 7)).

‡ See page 849.

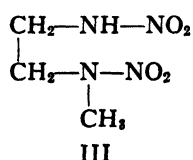
and one secondary group. The ratio of the predicted to the observed maximal molecular extinction coefficient of this compound is shown in the right hand

TABLE IV

ABSORPTION SPECTRA OF MIXED PRIMARY AND SECONDARY NITRAMINES
POSITION AND INTENSITY OF THE MAXIMA

Structure	Compound	Solvent	Absorption max.		E_{\max} obs.
			λ , Å	E_{\max} obs.	E_{\max} predicted
III	1,4-Dinitro-1,4-diazapentane	Ethanol	2375	12950	1.04
	Potassium salt of III	0.2 <i>N</i> HCl	2360	12200	0.99

column of Table IV. It should be noted that in the nitramines E_{\max} is closely the same in both ethanol and dioxane solutions.



The majority of both the primary and secondary nitramines that were available to us contained additional functional groups and the influence of these groups must be taken into consideration in evaluating the spectrometric data. It is well known that in compounds containing more than one chromophoric group the different chromophores will absorb more or less independently of one another, provided they are separated by at least one methylene group. In such compounds the observed absorption approximates closely to that which would be predicted from the sum of the absorptions associated with the separate chromophores.

In Tables II, III, and IV are included all primary and secondary nitramines in which the other nonconjugated functional substituents do not appear to influence the shape of the spectral curve. These substituents are summarized in Table V. It cannot be assumed, however, that these substituents will necessarily show no effects on the spectra of other nitramines; this may depend on the ratio of the number of such groups to the number of nitramine groups in the molecule. In the case of compounds containing the nitroxy group (—C—O—NO_2), together with nitramine groups, increases in the intensity of absorption at the nitramine maximum are observed that can be attributed to the effect of the nitroxy absorption (page 852). It is probable that some of the deviations from whole numbers in Column 6 of Tables II and III may be due to similar causes (page 857).

TABLE V

SUBSTITUENT GROUPS (R) WHICH MAY BE INTRODUCED INTO THE MOLECULES $R-CH_2-NH-NO_2$ AND $\begin{array}{c} R-CH_2 \\ | \\ N-NO_2 \\ | \\ R-CH_2 \end{array}$ WITHOUT SIGNIFICANTLY ALTERING THE SHAPE OF THE SPECTRAL CURVE

1. $-O-COCH_3$	7. $\begin{array}{c} -N- \\ \\ COCH_3 \end{array}$
2. $-O-NO_2$	
3. $NH_3^+ NO_3^-$	8. $\begin{array}{c} -N- \\ \\ COOC_2H_5 \end{array}$
4. $-Cl$	
5. $-OCH_3$	9. $-NH_3^+ Cl^-$
6. $-OC_2H_5$	

C. Spectra of Nitramines in Alkaline Solution

The hydrogen atom attached to nitrogen in the primary nitramine group has acidic properties, and it is therefore to be anticipated that in alkaline solution the spectrum of a primary nitramine may show a change attributable to the effect of ionization.

The spectra of several primary nitramines have been determined in the presence of sodium hydroxide solution (Table VI). The absorption spectrum

TABLE VI

ABSORPTION SPECTRA OF PRIMARY NITRAMINES IN ALKALINE SOLUTION

Structure	Compound	Solvent	Absorption max.		E_{\max} 8300
			λ , Å	E_{\max}	
XXII	Methylnitramine	N/4 KOH	2280	7600	0.90*
	N-(trimethylolmethyl)-nitramine	N NaOH	2360	8070	0.95*
	n-Butylnitramine	0.2 N NaOH	2325	8460	1.00
VI	2-Nitroxyethylnitramine	0.2 N NaOH	2290	6320	0.79
I	Ethylenedinitramine	0.2 N NaOH	2360	17100	2.02
	1,7-Dinitro-1,4,7-triazaheptane	N KOH	2275	18600	2.18
	Propylenedinitramine-1,2	0.2 N NaOH	2360	17240	2.03
XIX	Methylenedinitramine	0.2 N NaOH	2325	17100	2.02
	1,5-Dinitro-3-nitroso-1,5-diazapentane	0.2 N NaOH	2325	18400	2.16
XLIII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dihydrochloride	0.2 N NaOH	2310	16620	1.96
	1,5-Dinitro-3-methyl-3(methylenenitramine)-1,5-diazapentane	0.2 N NaOH	2325	28900	3.39

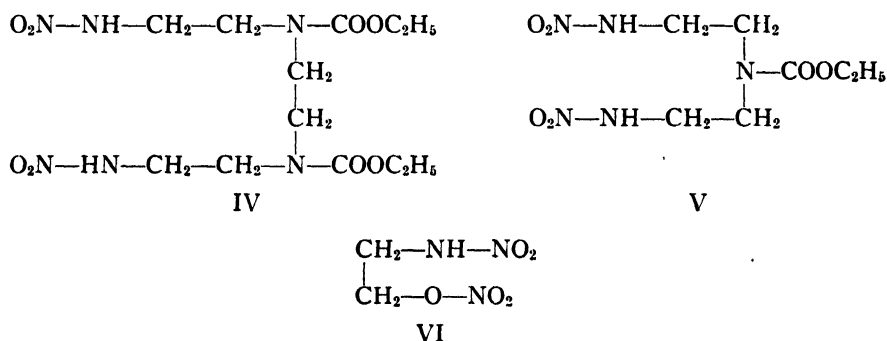
* Data privately communicated by Dr. Carmack (see references (6), (7)).

is changed but the alteration is relatively small. There is a significant increase in the intensity of absorption at the maximum, and the position of the maximum is shifted slightly to longer wave lengths (see Fig. 1, Curve B). The intensity at the maximum is a linear function of the number of primary nitramine groups in the molecule, and the molecular extinction constant is increased to 8500.

Secondary nitramines tend to be unstable in alkali, but in cases where the compounds were sufficiently stable to enable the spectra to be determined, the wave length of the maximum was unchanged from that observed in neutral solution. The intensities varied somewhat irregularly, but the variations were mostly small. In acid solution the spectra of both primary and secondary nitramines are the same as in neutral solution.

D. Distinction Between Primary and Secondary Nitramines

The difference in the molecular extinction constants of the primary and secondary nitramine groups suggests that such groups might be distinguished by ultraviolet spectrometry. As the difference in intensity is greater in alkaline than in neutral or acidic solution, the comparison should be made in the presence of alkali if the substance is sufficiently stable. Such characterization of the nitramine type from spectrometric data must be considered with some reserve, since in the case of three primary nitramines of known structure (IV, V, and VI) the extinction at the maximum is lower than would be calculated from the molecular extinction constant, and the intensity data actually fit better for a secondary nitramine (see also page 849).

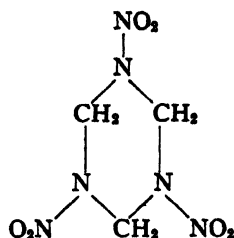


E. Comments on the Spectra of Individual Compounds

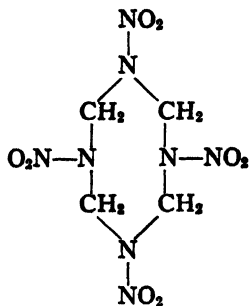
(i) 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)

The spectrum of RDX (VII) has been studied intensively in ethanol, methanol, dioxane, and water. It does not show the maximum in the neighborhood of 2300 Å, observed for most nitramines; instead there is an inflection near 2400 Å and the curve continues to rise slowly at shorter wave lengths. In water the slope in this region is slightly flatter than in methanol (Fig. 3 Curves A, B). The extinction coefficients in this flat region are lower than the values calculated for three secondary nitramine groups; this indicates

that the flattening of the curve is the result of a depression in the intensity of absorption and is not due to the superposition of additional absorption on the nitramine curve. (page 857).



VII



VIII

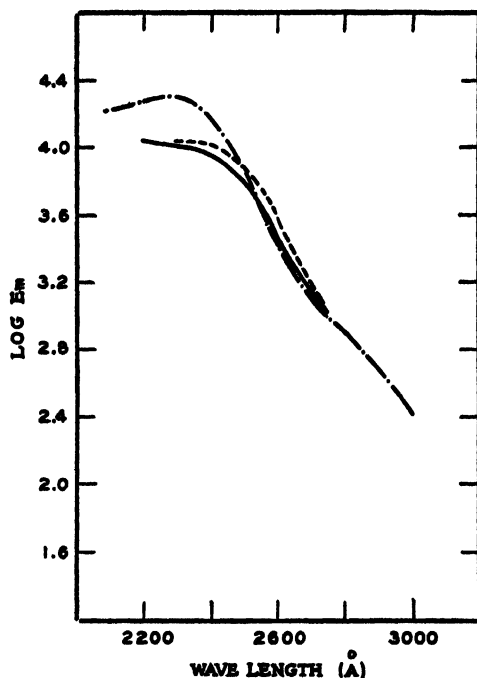


FIG. 3. 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX).

— Curve A. Solvent, methanol.

- - - Curve B. " water.

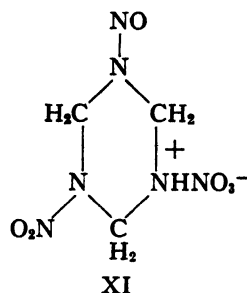
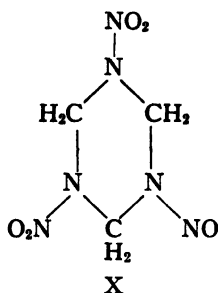
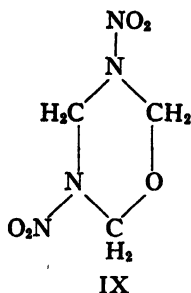
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX).

- · - · - Curve C. Solvent, methanol.

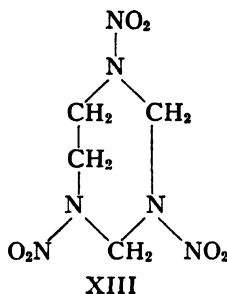
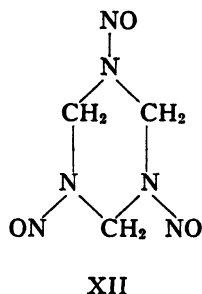
The spectrum of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) (VIII) (Fig. 3, Curve C) is normal, and the difference in shape of the curves of the two compounds is sufficient to allow the spectrographic assay of mixtures of RDX and HMX*. The spectra of RDX and HMX have also been recorded by Whitmore and Noll, whose curves agree with ours.

* Unpublished observation from these laboratories.

This flattening and depression of the absorption maximum has been observed also in the spectra of IX, X, XI (Fig. 13, Curves A, B). Trinitrosotrimethylene-triamine (XII) however gives a normal nitrosamine curve (page 850) and the triazacycloheptane derivative XIII gives a normal nitramine curve,



though the intensity is slightly low for three nitramine groups (Fig. 13, Curve C) (E_{\max} 14,900 \equiv 2.72 secondary nitramines).

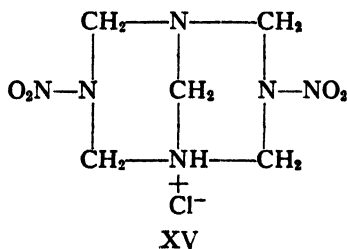
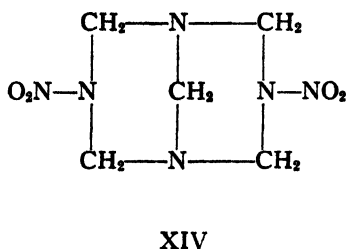


A flattening of the absorption maximum has also been observed in the spectrum of compound XLII (Fig. 18, Curve A) but in this case the effect can be reasonably attributed to the superposition of absorption from the nitrate groups on top of the nitramine absorption (see also page 859).

Among the primary and secondary nitramines in Tables II and III are several compounds that were obtained as intermediates or by-products in the preparation of RDX. In the case of most of these compounds the evidence of structure derived from the spectra agrees satisfactorily with the chemical data. In the case of the two compounds, XIV and XVII, some discrepancies occur and are discussed below.

(ii) Dinitropentamethylenetetramine (DPT)

The spectrum of DPT (XIV) is quite normal in neutral dioxane solution; there is a typical secondary



nitramine maximum (Fig. 4, Curve A) at 2410 Å with an extinction coefficient of 11,000. In 0.2 *N* hydrochloric acid, however, the maximum shifts to 2150 Å (Fig. 4, Curve B) and in no other secondary nitramine has a hypsochromic shift of this kind been observed on acidification. In the accepted

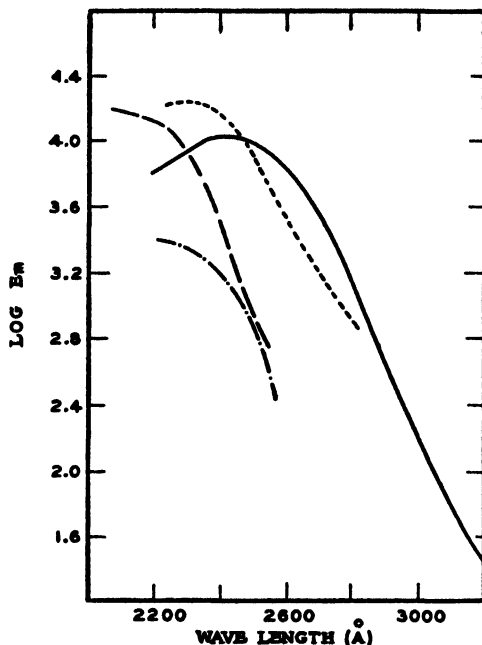


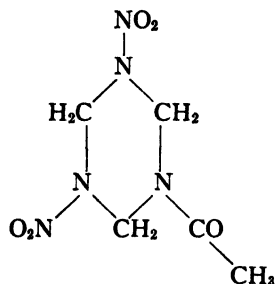
FIG. 4. *Dinitropentamethylenetetramine (DPT).*

- Curve A. Solvent, dioxane.
- - - - - Curve B. " 0.2 *N* hydrochloric acid.
- · - · - · - Curve C. Product from B at pH 9.
- · · · · Curve D. Solvent, 0.2 *N* sodium hydroxide.

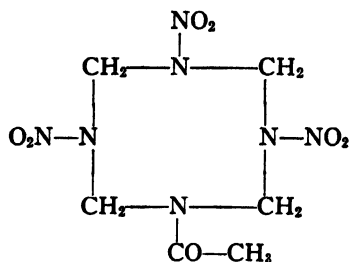
formula XIV there is a tertiary amino nitrogen atom, and the shift of the absorption maximum may be associated with the addition of a proton at this position (XV). However, as this basic nitrogen atom is separated from the nitramine chromophores by methylene groups, this explanation will hardly suffice, since the addition of a proton at this position cannot have any direct effect on the energies of the resonance states contributing to the structure of the nitramine groups. This spectrographic behavior can be reconciled with the accepted formula for DPT, if it be assumed that on the addition of dilute acid the DPT is decomposed, so that we are not dealing with a case of simple quaternary salt formation. This view receives some support from the observation that when such an acidified solution is subsequently brought to pH 9, the intensity falls off very considerably and the curve is not reproducible (Fig. 4, Curve C); the spectrum also differs considerably from that obtained when a neutral solution of DPT is made directly alkaline with 0.2 *N* sodium hydroxide (Fig. 4, Curve D).

(iii) (1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane) (TAX)

This substance was isolated by Wright and coworkers as a by-product from a Bachmann reaction carried out in the presence of a large excess of acetic anhydride (1). The analytical figures suggested a formula $C_6H_{10}O_6N_6$ or $C_5H_9O_5N_5$ and crystallographic analysis established that $C_5H_9O_5N_5$ was correct. The Franchimont test for the nitramine group was positive; analysis indicated the presence of one acetyl group, and tests for nitrate ions and nitroxy groups were negative. Wright and coworkers have proposed the structure XVI (1).



XVI



XVII

The spectrum of XVI is illustrated in Fig. 5. While this curve has the shape of a typical nitramine, the intensity at the maximum (E_m 6300 in ethanol; 6450 in dioxane) is much below that expected of a molecule containing two

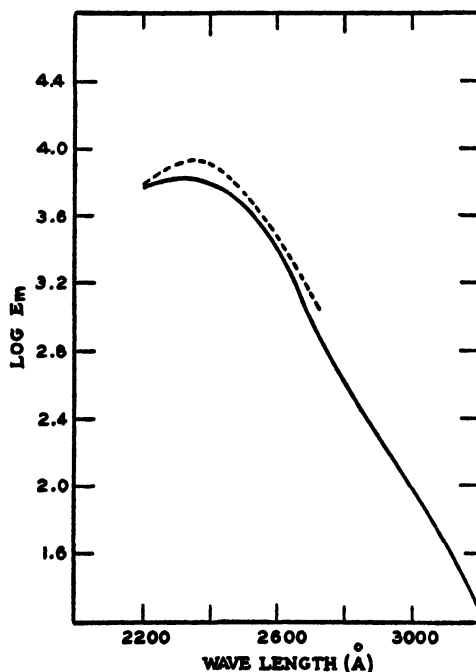


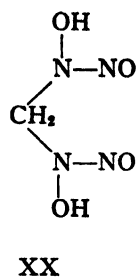
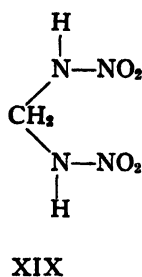
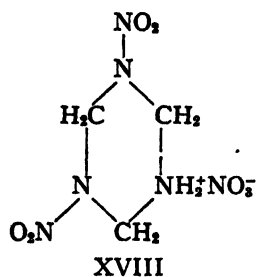
FIG. 5. 1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane.

————— Curve A. Solvent, ethanol.
 - - - - - Curve B. " 0.2 N sodium hydroxide.

secondary nitramine groups (E_m calc. 11,000) and fits more satisfactorily for one nitramine per molecule. Compound XVII with a structure somewhat analogous to that postulated for XVI gives a normal spectrum, and the intensity of the maximum agrees with that required for three secondary nitramine groups.

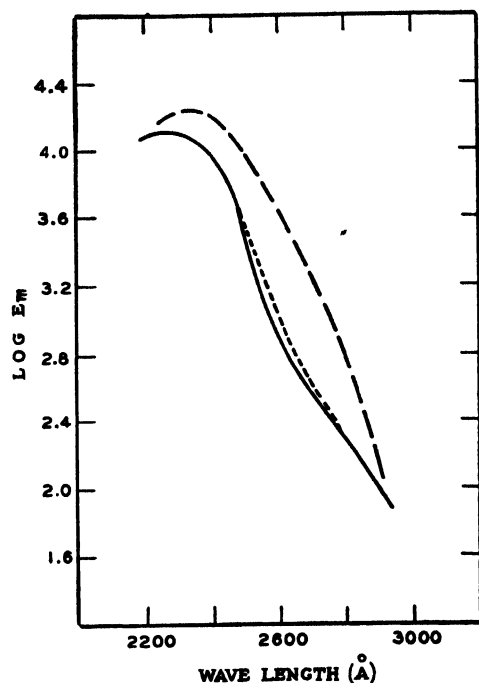
F. The Spectra of Methylenedinitramine Isomers

Considerable interest has been shown in the structure of two isomeric compounds of empirical formula $\text{CH}_4\text{N}_4\text{O}_4$. One of these was first prepared in 1895 by Traube by the condensation of acetone, sodium ethoxide, and nitric oxide (27) and is commonly referred to as the "Traube compound". An isomer has been obtained by J. K. N. Jones and coworkers (3) by the hydrolysis of 1,3-dinitro-1,3,5-triazacyclohexane-5-nitrate (XVIII) (PCX). It seems probable that the product of the latter reaction is the true methylenedinitramine (XIX) and the "Traube compound" is methylene-*bis*-nitrosohydroxylamine (XX).

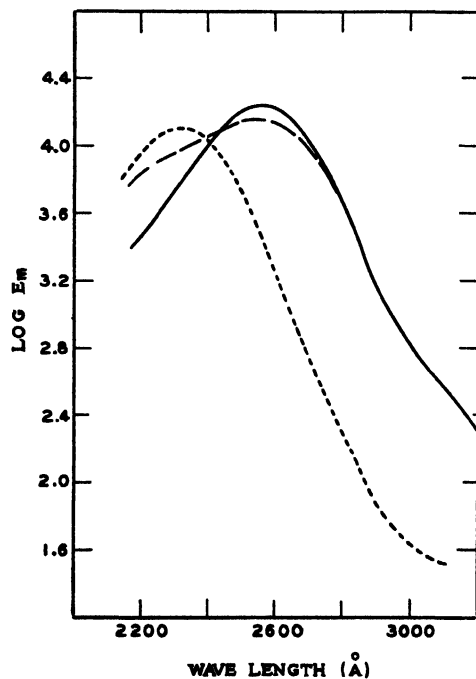


The ultraviolet absorption spectra of these isomers have also been investigated by Carmack and Leavitt (6) and by Garwood and J. K. N. Jones (9). Determinations of the spectrum of the product from the hydrolysis of XVIII in our laboratories showed it to possess the typical curve of a primary nitramine. The maximum was at 2260 Å and the extinction coefficient was 12,530 in ethanol solution, which corresponds to 1.80 nitramine groups per molecule (Fig. 6, Curve A). In 0.2 *N* sodium hydroxide solution the maximum was shifted to 2325 Å and the extinction coefficient increased to 17,100 (2.02 nitramine groups) (Fig. 6, Curve C).

The Traube compound is unstable in the free state and is usually prepared as the mono-ammonium salt or as the disodium salt. A solution of the free acid of the Traube compound was obtained by dissolving the mono-ammonium salt in *N* hydrochloric acid. The spectrum of this solution (Fig. 7, Curve C) has a maximum at 2310 Å with extinction coefficient of 12,600; this resembles closely the curve of the hydrolysis product of XVIII and is quite acceptable as the curve of a primary nitramine. In alkaline solution, however, the absorption maximum is at 2550 Å and such a large bathochromic shift on addition of alkali has not been observed in the spectra of primary nitramines of established structure. This is illustrated in the curves of Fig. 7 and Fig. 8. While the spectrum of the free acid of the Traube compound resembles that of a primary nitramine, the spectra of its salts are clearly anomalous.

FIG. 6. *Methylenedinitramine from hydrolysis of PCX.*

————— Curve A. Solvent, ethanol.
 - - - - - Curve B. " 0.2 N hydrochloric acid.
 Curve C. " 0.2 N sodium hydroxide.

FIG. 7. *Acid ammonium salt of the "Traube compound".*

————— Curve A. Solvent, N ammonium hydroxide.
 - - - - - " B. " water.
 " C. " N hydrochloric acid.

The resemblance of the spectrum of the free acid from the Traube ammonium salt to that of the product from the hydrolysis of XVIII suggested that the Traube compound might be undergoing isomerization in acid solution, but this was disproved by the following experiment. The absorption spectrum of the disodium salt of the Traube compound was first determined in aqueous solution (Fig. 8, Curve A); the solution was then acidified with 0.2 *N* hydrochloric acid and the curve of the resulting free acid measured (Fig. 8, Curve B).

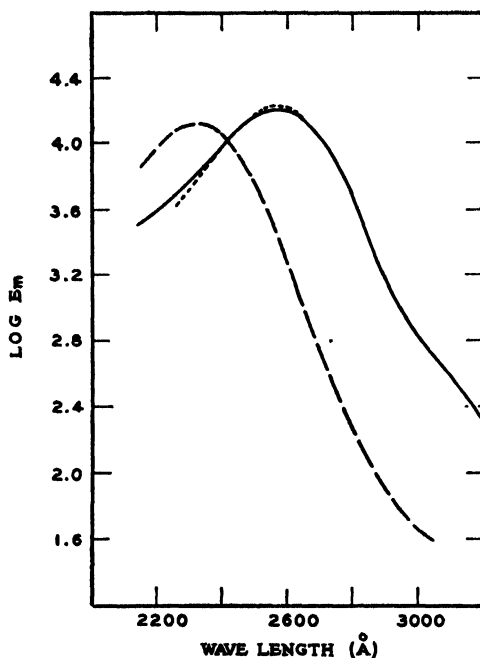


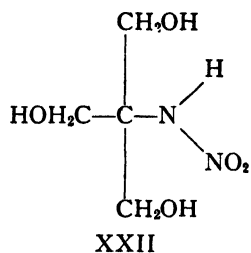
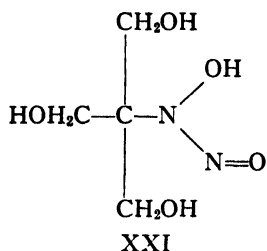
FIG. 8. Disodium salt of the "Traube compound".

—————	Curve A.	Solvent, water.
- - - - -	" B.	" 0.2 <i>N</i> hydrochloric acid.
· · · · ·	" C.	" product from B in <i>N</i> potassium hydroxide.

This acid solution was then made alkaline with *N* potassium hydroxide and the spectrum of the resultant salt was found to be identical with that of the original salt (Fig. 8, Curve C). These experiments showed that, although the free acid from the ammonium salt (or the disodium salt) of the Traube compound and the hydrolysis product of XVIII have similar spectra, the molecules differ in structure, since on addition of alkali the salt of the Traube compound has the maximum well displaced to longer wave lengths while that of the hydrolysis product of XVIII shows only a slight shift.

These observations have been substantiated by the results of Carmack and Leavitt (6) who have compared the spectrum of the Traube compound in neutral and in acid solution with the spectrum of a nitrosohydroxylamine derivative of established structure. The two model isomeric compounds,

N-(trimethylolmethyl)-nitrosohydroxylamine and N-(trimethylolmethyl)-nitramine (XXI, XXII), were synthesized by Cason and Prout (7) for this purpose.



The spectrum of the nitrosohydroxylamine compound (XXI) resembles that of the Traube compound very closely, both in neutral and in acid solution, and supports the formulation of the latter as (XX). The spectra of both methylenedinitramine isomers have been investigated also by Garwood and J. K. N. Jones (9), who also concluded that the product from the Traube reaction is a methylene-*bis*-nitrosohydroxylamine.

From the Traube compound it is possible to obtain two isomeric dimethyl esters. One of these (the α -methyl ester) is a white crystalline compound, with a spectrum very similar to that of the free Traube acid (Fig. 9). The β -ester is pale yellow and the spectrum shows a well developed low intensity maximum at 3800 Å. This long wave length, low intensity maximum has

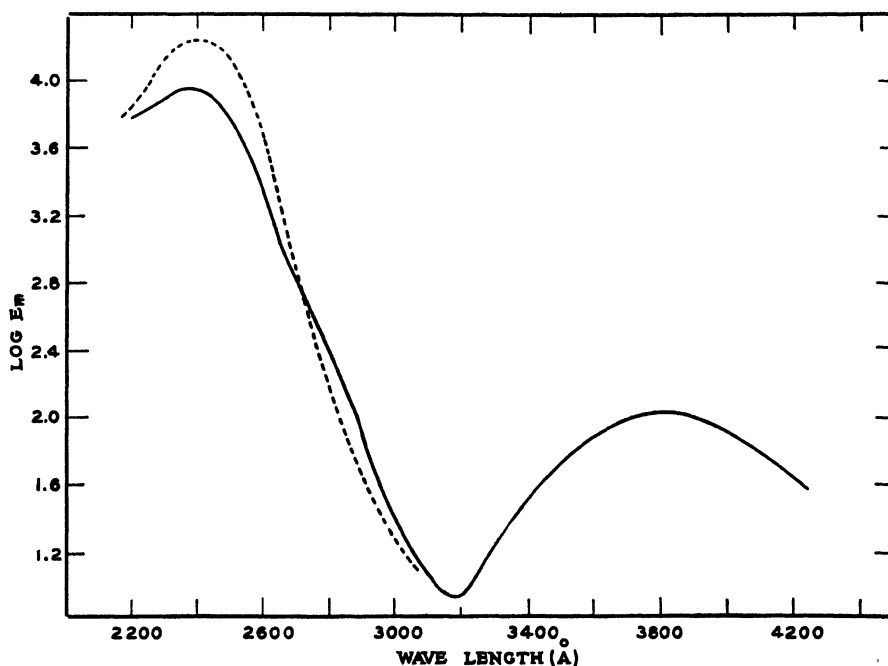


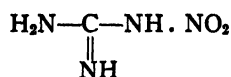
FIG. 9. Esters of the "Traube compound".

----- Curve A. α -Methyl ester (solvent, ethanol).
 ————— " B. β -Methyl ester (" ").

been observed in many compounds containing a nitroso group, and the structure and spectrum of this ester are discussed further on page 852. Garwood and J. K. N. Jones (9) also determined the spectra of these isomeric esters, and their curves are in good agreement with ours.

G. Nitramines Containing Conjugated Substituents

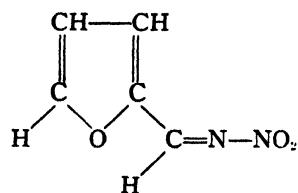
If a compound should contain a nitramine group together with a second chromophoric group so placed that a conjugated system extends from the nitramine group to the second substituent, radical changes in the spectrum would be anticipated. Nitroguanidine (XXIII), nitrourethane (XXIV), and furfural nitramide (XXV) are compounds of this type.



XXIII



XXIV



XXV

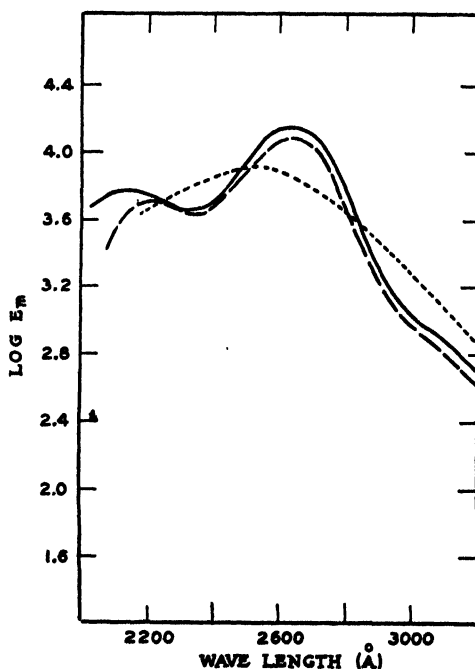


FIG. 10. Nitroguanidine.

— Curve A. Solvent, water.
 - - - " B. " N hydrochloric acid.
 . . . " C. " N sodium hydroxide.

Nitroguanidine (Fig. 10) has a spectrum in neutral solution with two maxima; on addition of alkali this is altered and only one maximum is observed. The spectrum of nitrourethane (Fig. 11) possesses, in neutral solution, a single maximum of high intensity (Curve C); in 0.2 N sodium hydroxide two maxima

appear (2600 and 2100 Å) and the spectrum closely resembles that of the potassium salt in water (Curve A); in 0.2 *N* hydrochloric acid the spectrum

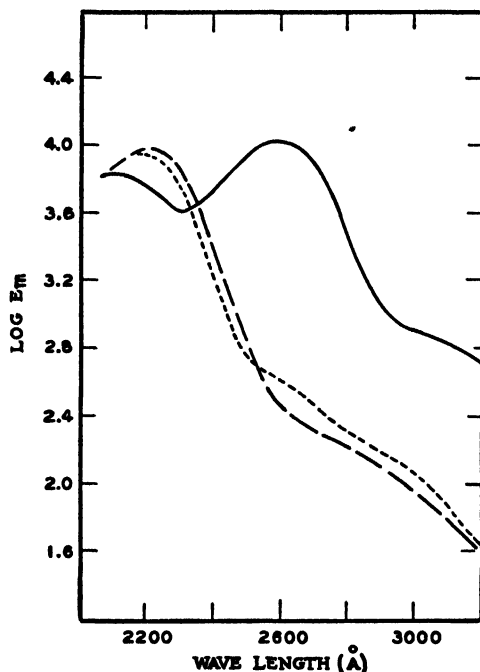


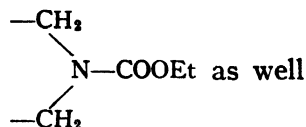
FIG. 11. Nitrourethane.

— Curve A. Potassium salt in water.
 - - - " B. Solvent, 0.2 *N* hydrochloric acid.
 - · - · " C. " ethanol.

is the same as in water. The spectrum of nitrourethane in alkaline solutions bears a close resemblance to that of a neutral solution of nitroguanidine. Ethanol solutions of furfural nitramide (Fig. 12) show maxima at 3200 and 2700 Å.

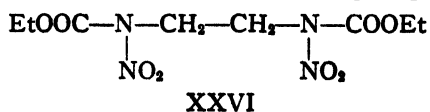
H. Compounds Containing Carboethoxy Groups

Two compounds (IV, V) containing the grouping



as primary nitramine groups are recorded in Table III. In these the carboethoxy substituents are not conjugated with the nitramine groups; the shapes of the curves are similar to that of simple nitramines, but the intensities are appreciably low. The calculated values for the absorption maxima of both IV and V based on the molecular extinction constant is 14,000, while the observed values are 11,500 and 11,200 respectively.

Compound XXVI contains two carboethoxy groups substituted



directly into the nitramine chromophore. The spectrum is of the typical nitramine type, but in this case also the intensity is slightly low (see Table II). This compound should be compared with nitrourethane (Fig. 11).

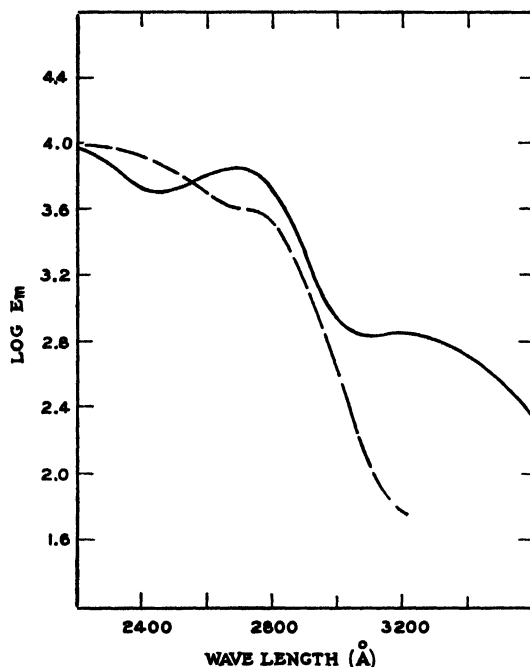


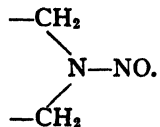
FIG. 12. *Furfural nitramide.*

————— Curve A. Solvent, ethanol.
 - - - - - " B. " 0.2 N sodium hydroxide.

III. The Spectra of Nitroso Compounds

A. Nitrosamines

The number of nitrosamines included in these studies has been relatively small; they are all of the secondary type, containing the grouping



These compounds contain either a nitrosamine group alone, or a nitrosamine group together with a nitramine group. They show two absorption maxima, one in the same region as the nitramine maximum and of the same order of intensity, another at 3600 to 3850 Å with a molecular extinction coefficient of the order of 100. This low intensity maximum may show evidence of fine structure resolution. It is the end absorption of this band that imparts a pale yellow color to many nitrosamines. The intensities of absorption at the maxima appear to vary appreciably from one nitrosamine to another, and with the rather limited data available it does not seem possible to establish any simple relations between the number of nitramine and nitrosamine groups

in the molecule and the intensities at the maxima. These spectra are summarized in Table VII. Typical examples are illustrated in Fig. 13, Curves B, C, and D.

TABLE VII
ABSORPTION SPECTRA OF SECONDARY NITROSAMINES
POSITIONS AND INTENSITIES OF THE MAXIMA

Structure	Compound	Solvent	Absorption maxima			
			λ_{\max}	E_{\max}	λ_{\max}	E_{\max}
X	1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane	Ethanol	*		3650	48
	N-Nitro-N'-nitrosopiperazine	Ethanol	2420	12900	3600	123
XI	1-Nitroso-3-nitro-1,3,5-triazacyclohexane-5-nitrate	Ethanol	*		3740	69
		Benzene			3850	66.3
	1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	Acetone				
		Ethanol	2280	18750	3760	69
XII	Dinitrosopentamethylene-tetramine	Ethanol	2300	10740	3675	115
	1,3,5-Trinitroso-1,3,5-triazacyclohexane	Ethanol	2350	13200	3700	174
					3820	166

* These compounds show a plateau only in this region (see page 841).

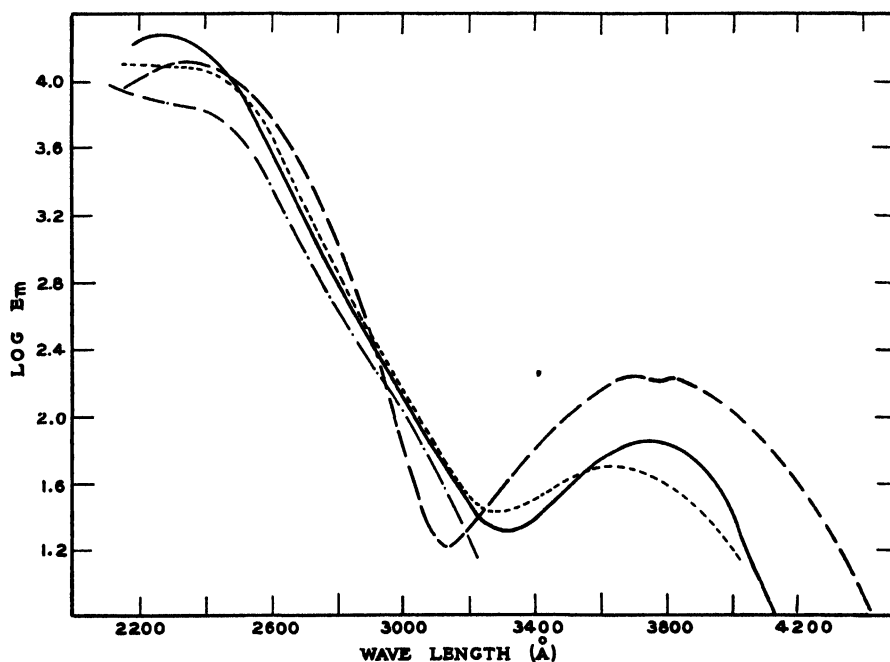
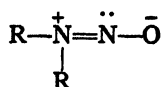
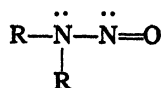


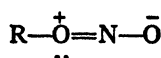
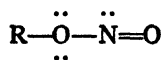
FIG. 13.

- Curve A. 1-Oxa-3,5-dinitro-3,5-diazacyclohexane.
 ----- " B. 1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane.
 -.-.-.- " C. 1,3,5-Trinitroso-1,3,5-triazacyclohexane.
 _____ " D. 1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane.
 Solvent, ethanol.

The absorption maximum at 3600 to 3850 Å in the nitrosamine spectrum resembles similar structure in the spectra of the alkyl nitroso compounds such as amyl nitrite (2, 5, 9), and octyl nitrite (23). In both types of compounds the resonating structures which probably predominate show some similarity (XXVII - XXVIII).



XXVII Nitrosamine resonance

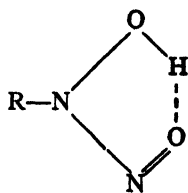


XXVIII Nitrosoalkane resonance

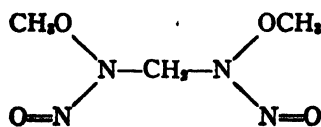
B. Nitrosohydroxylamines

When the close similarity of the spectrum of the "Traube compound" to that of a typical nitramine was first observed (see page 847), the absence of a long wave "nitroso band" was considered fairly conclusive evidence *against* the formulation of that compound as a nitrosohydroxylamine derivative (XX). Later, Carmack, and Leavitt (6) reported the absorption spectrum of a nitrosohydroxylamine (XXI) synthesized by Cason by an unequivocal method and it was noted that the long wave "nitroso band" was absent from the spectrum of this compound also.

The disappearance of the "nitroso band" in these hydroxy derivatives may be the result of hydrogen bonding as shown in XXIX. The β -methyl ester of the Traube compound, which has a typical nitrosamine spectrum, may be represented by XXX, in which the hydrogen bonding has been destroyed by the introduction of the methyl group.



XXIX



XXX

IV. The Spectra of Nitroxy Groups and Nitrate Ions

The nitrate ion (NO_3^-) and the nitroxy group ($-\text{O}-\text{NO}_2$) give rise to quite different spectra. The nitrate ion spectrum has a very low intensity maximum near 3000 Å (19), and the absorption rises very steeply in the further ultra-violet region (Fig. 14, Curve B). The nitroxy group gives a spectrum in which there is no maximum, but a sharp inflection occurs near 2600 Å (Fig. 14, Curve A). The spectrographic data for compounds containing ionized nitrate groups which we have examined are summarized in Table VIII, and the data for the nitroxy inflection are listed in Table IX. For the ionized nitrate

group a molecular extinction constant of 7.6 at the maximum has been assigned. For the nitroxy inflection the assignment of a similar constant to the intensity at the point of inflection is hardly justified on the basis of the

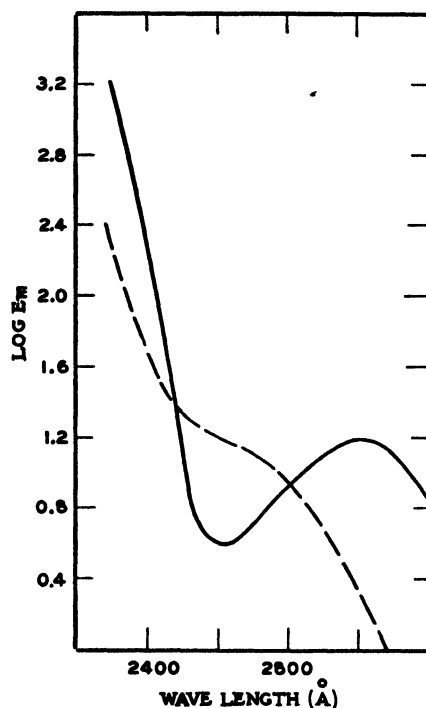


FIG. 14.

--- Curve A. Nitroxyethane (solvent, ethanol).
 ——— " B. Ethylenediamine dinitrate (solvent, water).

TABLE VIII

ABSORPTION SPECTRA OF COMPOUNDS CONTAINING NITRATE IONS
 POSITION AND INTENSITY OF THE MAXIMUM

Compound	Solvent	Absorption max.		$E_{\max}/7.6$
		λ , Å	E_{\max}	
Ammonium nitrate	Water	3015	7.6	1.00
Hexamine mononitrate	Water	3015	9.1	1.20
Hexamine-(N-acetylaminomethyl)-nitrate	Water	3015	7.8	1.05
Ethylenediamine dinitrate	Water	3015	15.0	1.95
Hexamine dinitrate	Water	3015	18.6	2.35

data at present available; however, for the purpose of the calculations described in the following paragraph we have assumed the value of 14.8 at 2650 Å, taken from the curve for nitroxyethane.

TABLE IX

ABSORPTION SPECTRA OF COMPOUNDS CONTAINING NITROXY GROUPS
POSITION AND INTENSITY OF THE POINT OF INFLECTION

Compound	Solvent	Absorption at point of inflection	
		λ , Å	E_{molar}
Nitrosoethane	Ethanol	2650	14.8
2,3,4-Triacetyl- α -methyl-D-glucoside-6-nitrate	Methanol	2650	20.2
α -Methyl-D-glucose-6-nitrate	Water	2650	19.0
2,3,4-Trimethyl- β -methyl-D-glucose-6-nitrate	Ethanol	2650	21.4
3,4,6-Triacetyl- β -methyl-D-glucose-2-nitrate	Methanol	2700	26.2

V. Spectra of Compounds Containing Mixed Groups

A. Nitroso Groups and Nitrate Ions

In Figs. 15 and 16 are illustrated the spectra of four compounds that contain both nitrate ions and nitroso groups. The shape of these curves is quite characteristic, and the question arises whether the number of each type

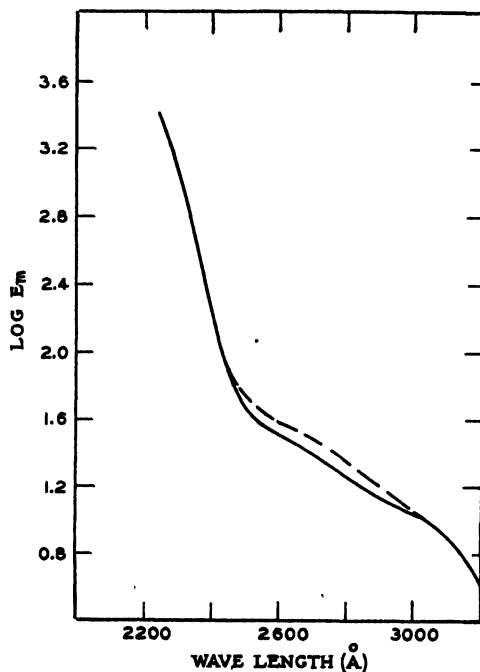


FIG. 15.

- Curve A. 1,5-Dinitroso-3-azapentane nitrate (XXXIII).
 - - - - - " B. 2,6-Dinitroso-4-azaheptane nitrate (XXXII).
 (Solvent, water).

of group in the molecule can be deduced from the appearance of the absorption curve. Comparison of the spectra of nitroxyethane (Fig. 14, Curve A) and ethylenediamine dinitrate (XXXI) (Fig. 14, Curve B) shows that the

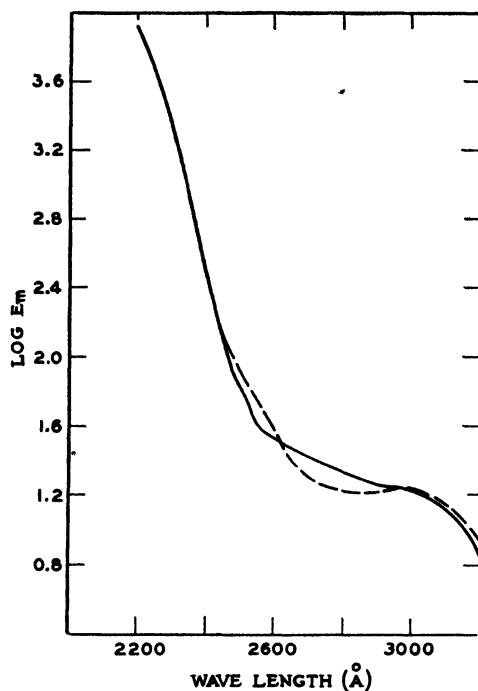


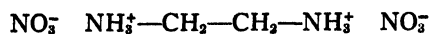
FIG. 16.

— Curve A. *1,8-Dinitroxy-3,6-diazaoctane dinitrate (XXXIV).*
 - - - - - " B. *1-Nitroxy-3,6-diazaheptane dinitrate (XXXV).*
 (Solvent, water).

minimum in the nitrate ion curve occurs in the same region as the inflection in the spectra of nitroxy compounds. In compounds containing both groups, but no other chromophoric centers, the shape of the curve should vary considerably with the ratio

$$\frac{\text{Number of nitroxy groups}}{\text{Number of nitrate ions}}$$

in the molecule. The over-all intensity should also vary with the total number of groups present, so that it should be possible from an analysis of the shape and position of the absorption curve to determine the actual number of each type of group present.



XXXI

As yet, insufficient data on compounds containing both types of groups are available to establish this with any certainty. In Table X we have

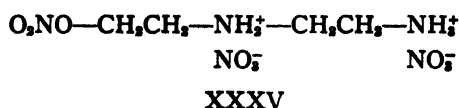
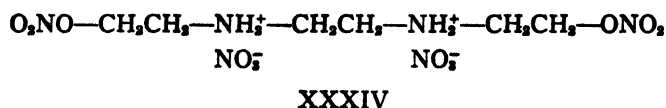
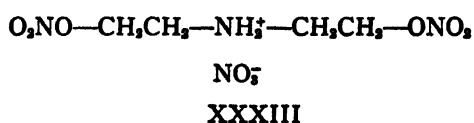
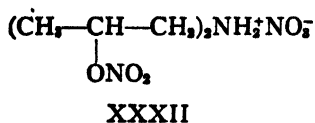
calculated the ratios of the extinction coefficients; $\frac{E_{2650}}{E_{3020}}$ for the four compounds XXXII to XXXV, and compared these with the ratios calculated on the basis of molecular extinction constants of 7.6 at 3020 Å and 1.9 at 2650 Å for the

TABLE X

ANALYSIS OF SPECTRA OF COMPOUNDS CONTAINING BOTH NITRATE IONS AND NITROXY GROUPS

Compound	Ratio ($-\text{O}-\text{NO}_2$) (NO_2)	Extinction coefficient predicted from molecular extinction constants			Extinction coefficient observed		
		E_{2650}	E_{3020}	$\frac{E_{2650}}{E_{3020}}$	E_{2650}	E_{3020}	$\frac{E_{2650}}{E_{3020}}$
XXXII	$\frac{2}{1}$	31.5	11.4	2.76	34.6	10.5	3.29
XXXIII	$\frac{2}{1}$	31.5	11.4	2.76	28.2	9.6	2.94
XXXIV	$\frac{2}{2}$	33.4	19.0	1.75	30.2	17.4	1.73
XXXV	$\frac{1}{2}$	18.6	17.1	1.08	25.0	17.8	1.40

nitrate ion group, and 1.9 at 3030 Å and 14.8 at 2650 Å for the nitroxy group. The calculated values for the ratio E_{2650}/E_{3020} vary from 1.08 for an ester/ion ratio of 1/2, to 2.76 for an ester/ion ratio of 2/1.



These results give promise that a spectrographic method for the simultaneous determination of the number of nitroxy and nitrate ion groups in a molecule may be developed, but the method must be tested on more compounds of known structure.

B. Nitramine and Nitroxy Groups

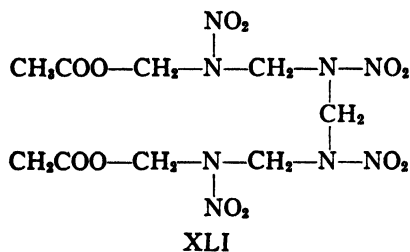
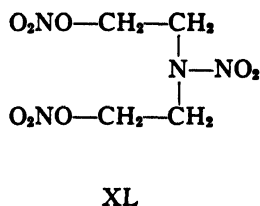
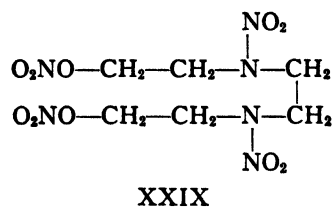
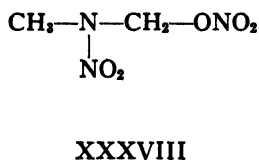
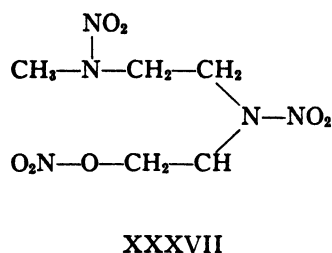
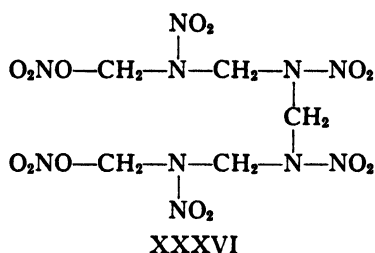
In compounds containing both nitramine and nitroxy groups, the nitroxy inflection at 2650 Å does not produce any apparent change in the shape of the absorption curve. This is true even when the molecule contains two

nitroxy groups and only one nitramine group (XL). In compound XXXVI there is a slight inflection at 2750 Å (Fig. 17, Curve B), but a similar inflection is present also in the spectra of other nitramine compounds that do not contain nitroxy groups, e.g., XLI (Fig. 17, Curve A).

It is probable that the nitroxy group does have a secondary effect on the intensity of the nitramine maximum, as the nitroxy chromophore produces rapidly increasing absorption in this region of the spectrum. In Table XI the spectra of five compounds (XXXVI–XL) containing both secondary nitramine and nitroxy groups are arranged in increasing order of the ratio

$$\frac{\text{Number of nitroxy groups}}{\text{Number of nitramine groups}}$$

Except for the compound in which this ratio is 0.5, the observed



intensity of the nitramine maximum is higher than that calculated from the molecular extinction constant, and this discrepancy increases with increase in the above ratio.*

C. Nitrate Ions and Nitramine Groups

The absorption maximum at 3015 Å associated with the nitrate ion is of such low intensity that it is completely "swamped" by the end absorption of

* Note however that in 2-nitroxyethylnitramine, which contains one nitroxy and one primary nitramine group, the intensity observed for the primary nitramine maximum is sensibly diminished (Table II).

the nitramine band, e.g., in the spectrum of XVIII there is no sign of nitrate ion absorption. At short wave lengths, however, the nitrate ion curve rises very steeply, and it may be significant that the spectrum of compound XLII

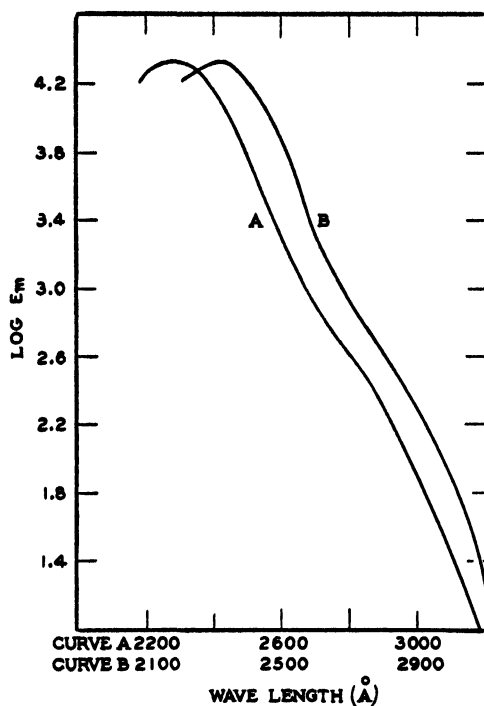


FIG. 17.

Curve A. 1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (XLI).

" B. 1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (XXXVI).
(Solvent, dioxane).

TABLE XI

EFFECT OF NITROXY GROUP ON THE INTENSITY OF THE SECONDARY NITRAMINE MAXIMUM

Compound	Ratio Nitroxy groups Nitramine groups	E_{\max}		$\frac{E_{\max. \text{ obs.}}}{E_{\max. \text{ calc.}}}$
		Calc.	Observed	
XXXVI	$\frac{2}{4}$	22,000	21,900	1.00
XXXVII	$\frac{1}{2}$	11,000	11,850	1.07
XXXVIII	$\frac{1}{1}$	5,500	6,700	1.23
XXXIX	$\frac{2}{2}$	11,000	12,000	1.10
XL	$\frac{2}{1}$	5,500	7,350	1.34

shows an inflection in the curve instead of a maximum (Fig. 18, Curve A), whereas with the corresponding chloride XLIII the ordinary nitramine maximum is observed (Fig. 18, Curve B.).

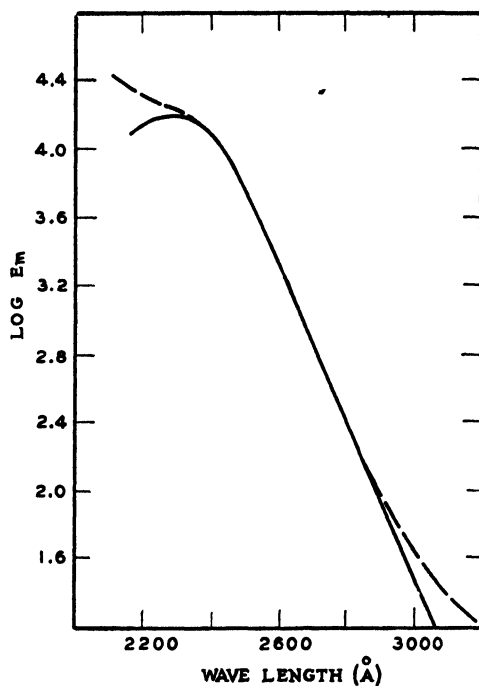
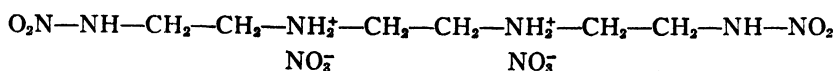
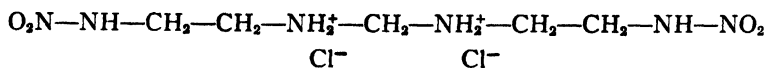


FIG. 18.

- — — — — Curve A. 1,10-Dinitro-1,4,7,10-tetrazadecane dinitrate (XLII).
 ————— “ B. 1,10-Dinitro-1,4,7,10-tetrazadecane dihydrochloride (XLIII).
 (Solvent, water).



XLII



XLIII

VI. Experimental

The spectra were measured on a Beckman model D.U. ultraviolet spectrometer; a slit width of 20 Å was employed between 2100 and 2350 Å and of 10 Å at longer wave lengths. The compounds were analytically pure samples. In no case was any evidence of reaction with the solvent or photochemical change observed.

VII. Concluding Remarks

The compounds included in this survey were selected mainly on the basis of their ready availability and because of their bearing on the elucidation of

the structure of compounds of specific interest in connection with the chemistry of RDX. Certain qualitative and quantitative relations between the chemical structure and the absorption spectra were observed. These results suffice to indicate that a more comprehensive survey of the ultraviolet absorption spectra of nonaromatic nitrogen containing compounds would probably lead to the establishment of additional correlations which could be of considerable help in the determination of the structure of nitrogenous compounds, including compounds from biological sources. Such a survey might profitably include the alkyl nitrites and the nitrite salts of organic acids as well as C-nitro and C-nitroso compounds.

The infrared absorption spectra between 4000 and 850 cm^{-1} of many of the compounds discussed here have been determined also and will be described in a later publication.

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SOME PROPERTIES OF CESIUM-AMMONIA SOLUTIONS¹

By J. W. HODGINS

Abstract

Measurements of vapor pressure, liquid density, and electrical conductance were made on solutions of cesium in liquid ammonia. The solutions differ from those of the other alkali metals in that there is no indication of liquid-liquid phase separation for concentrations 0.04 *N* to 7 *N*. Experiments on rings of solution frozen in liquid nitrogen make it appear unlikely that the system is superconducting at 77° K.

Introduction

Considerable investigation has been carried out recently (1-3, 6, 7, 9, 10, 16-22) on the characteristics of solutions of alkali metals and alkaline earth elements in liquid ammonia, with particular regard to their electrical conductance at low temperature. Much of the renewed interest in these solutions was occasioned by the report of R. A. Ogg, Jr. (20) on the persistence of currents induced in rings of frozen solutions of sodium in liquid ammonia. This phenomenon was regarded as evidence of superconductivity in the frozen solution at temperatures up to about 180° K., a very high temperature compared to the transition temperature heretofore observed for any metal or alloy.

The only experiments confirming the observation of these persistent currents were reported by the author in 1946 (10), although the technique of these experiments differed from that of Dr. Ogg. Also the strength of the current produced was less and of shorter duration, and the observations were all made at 90° K. Further comment will be made on these experiments in a later note.

Since the persistent currents observed with frozen sodium solutions were so feeble and so short-lived, and particularly since their appearance was so sporadic, it was decided, on taking up the study again, to examine the frozen solutions of other alkali metals for the persistence of an induced current. Lithium had already yielded negative results, and cesium was chosen for the study, its low ionization potential being an additional reason for its choice. Since the only positive answers with the sodium solution were obtained when the concentration of the solution was in the region of liquid-liquid phase separation (upper consolute temperature = -41.5° C. at a mole ratio $\text{NH}_3 : \text{Na} = 25 : 1$), it was first necessary to establish the concentration region within which liquid-liquid phase separation occurs for the cesium-ammonia solution. It was also found desirable to know the solubility of the metal in ammonia, the vapor pressure of the solutions, the density of the solutions, and the electrical conductance.

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Experimental

(A) APPARATUS

1. Determination of Vapor Pressure of Cesium-ammonia Solutions

An isothermal curve of vapor pressure as a function of concentration was required for three reasons. First, in subsequent experiments, it gave a convenient method of determining the concentration. Second, the curve would indicate, by a flat portion parallel to the concentration axis the region where two liquid phases were present. Third, the lower portion of the curve will become parallel to the concentration axis when the ammonia is saturated with cesium; this gives the solubility.

Since cesium is relatively rare, early attempts were made to combine the measurements of vapor pressure with those of conductance, but manipulative considerations indicated that these determinations would be better carried out separately. The plan for the vapor pressure measurements was to start with the strongest solution to be dealt with, and progressively dilute it with ammonia, a vapor pressure determination being made after each dilution.

Anhydrous ammonia (Matheson Alkali Company, East Rutherford, N.J.) was poured under pressure into a smaller cylinder to which had been added about 50 gm. of freshly cut sodium. This small cylinder was of the type designed by Kraus, and indeed was procured from Brown University. The sodium ensured the absolute dryness of the ammonia, and, after all the hydrogen had been blown off, the ammonia was added directly to the vacuum system from the cylinder. A sintered glass disk (*H*, Fig. 1) was inserted in the line to filter out any particles of sodamide that might be carried in the ammonia stream.

Metallic cesium (A. D. McKay Co., New York) was distilled in a weighed apparatus and sealed into frangible glass ampoules, to be broken *in vacuo* by a magnetic hammer as required.

The vapor pressure apparatus is illustrated in Fig. 1. *A* is a pressure release that allows ammonia to escape when its pressure exceeds a predetermined value. The escaped ammonia is absorbed in the water above the mercury in the blowoff. *C* is a calibrated volume (5440 ml.), *D* is the cell in which the cesium solution was prepared, and *E* a glass plunger activated by the solenoid *F* (a piece of iron is sealed into the shaft of *E*). The plunger is suspended on a steel spring, and is used as a stirrer by the application of an intermittent current to the solenoid, using an electronic interrupter as the source. The temperature of the solution in the tube is obtained by means of a calibrated thermocouple (*T.C.*) in a well dipping into the solution. Potentials were read on a Rubicon High Precision potentiometer, with a sensitivity of $0.5 \mu\text{v}$. Vapor pressures were read on manometer *G*, furnished with a mirror scale. All the volume elements of the apparatus were calibrated before use, and corrections were applied to the solution concentrations wherever the volume of vapor in the lines became significant.

All the vapor pressure measurements were performed at -50°C. , a temperature judged to be high enough to permit sufficiently large pressure readings, and possibly low enough to be below the consolute temperature for liquid-liquid phase separation, when the vapor pressure would be independent of

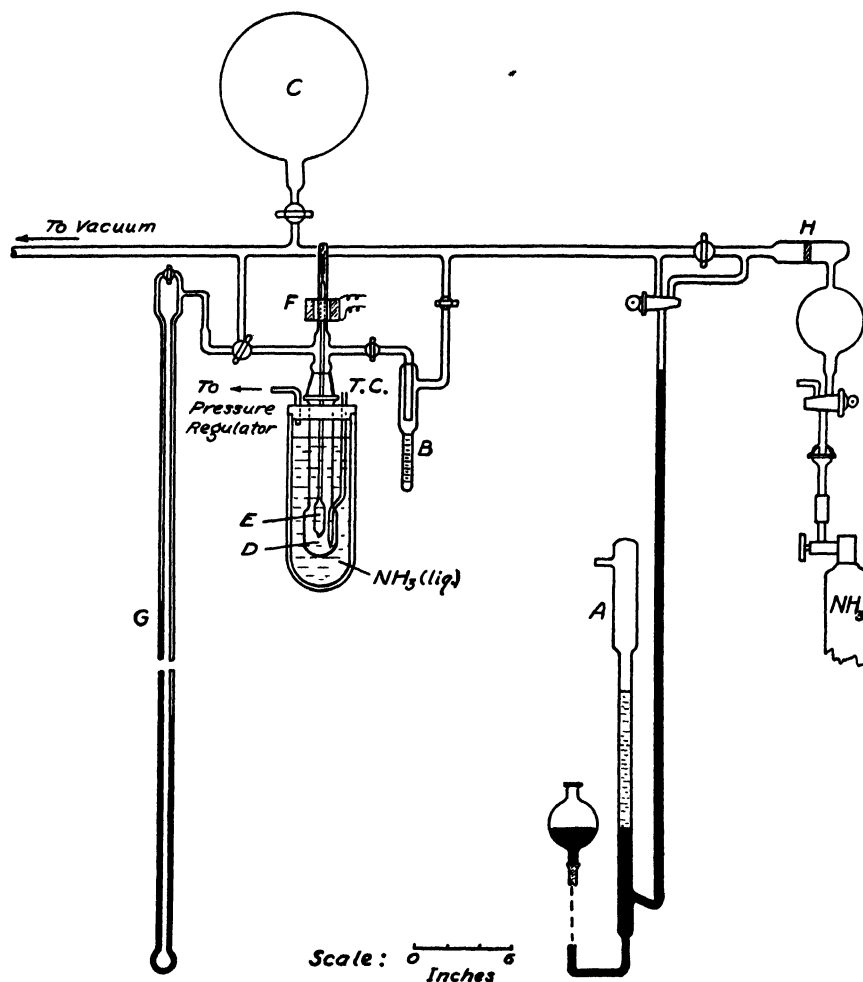


FIG. 1. Apparatus for measuring vapor pressures.

over-all concentration. The temperature of -50°C. was maintained by boiling liquid ammonia under reduced pressure in a Dewar flask around the vapor pressure tube. The Dewar flask was sealed to the rubber collar around the vapor pressure tube with plasticine (since it had to be removed frequently) and the pressure above the liquid ammonia reduced by means of a glass aspirator pump. When the vapor pressure was reached corresponding to -50°C. (311 mm.) a regulator took over and maintained the pressure constant. This manostat made it possible to hold any temperature between -35°C. and -70°C. constant to $\pm 0.02^{\circ}\text{C.}$

For the determination reported here, three ampoules containing a total of 3.825 gm. of pure cesium were put into tube *D*, which was evacuated. The

ampoules were broken by the magnetically operated plunger *E*. The required quantity of ammonia, previously measured in trap *B* and a calibrated bulb, was condensed into tube *D*, which was refrigerated in liquid air. The flask of liquid air around *D* was replaced by a flask of liquid ammonia, a seal was made with the rubber collar, and the manostat put into operation. The solution was stirred, and vapor pressure readings were made when the temperature was steady at -50°C .

This procedure was repeated for each point on the vapor-pressure curve by adding the appropriate quantity of ammonia necessary to attain the dilution desired. After vapor pressures had been recorded for 12 concentrations, all the ammonia was distilled from the cesium and the total quantity of ammonia added in one operation to give a concentration corresponding to the thirteenth point on the curve. No discontinuity was observed in the curve and thus the results were regarded as valid. As a final check on concentration the cesium was converted at the conclusion of the experiment to the ethoxide, water was added, and the hydroxide solution evaporated to dryness to expel remaining traces of ammonia. Determination of the cesium by titration with standard acid resulted in excellent agreement with the original quantity of cesium used.

2. Measurements of Density

Sodium solutions in liquid ammonia show a rather large increase in specific volume (14). That is, the total volume of solution is considerably higher than the sum of the volumes of its two constituents. Accordingly, it was of interest to determine whether the same expansion is characteristic of cesium solutions, and this determination was accomplished by measurements of the solution densities.

The densities were measured at -50°C ., using a Westphal balance in an apparatus similar to that used by Kraus, Carney, and Johnson (14). A diagram of the apparatus is given in Fig. 2. The float (volume = 2.62 ml. at -50°C .) was suspended in the solution by means of a platinum wire (No. 38 B.S.S.). When it was necessary to evacuate the tube a closure was obtained by squeezing a piece of gum rubber tube around the wire by means of a pinch-clamp—a device that gives a surprisingly tight seal.

A solution of known concentration was produced in the bottom of the tube by adding a weighed quantity of cesium *in vacuo* and distilling in the appropriate quantity of ammonia. With the solution held at -50°C . by the boiling ammonia cryostat, the solution was stirred by introducing a few bubbles of hydrogen through tube *A*, the hydrogen being added until the tube had reached atmospheric pressure. During the actual weighing of the float it was, of course, necessary to exclude air from the solution. Accordingly, when the pinchclamp closure around the wire at the top of the tube was opened, a brisk flow (100 ml. per min.) of hydrogen-ammonia was started through *B* and *C* (Fig. 2) to maintain a positive pressure at the mouth of the tube. The flow rates of hydrogen and ammonia were so regulated that the partial pressure of ammonia in the gas mixture corresponded to the vapor

pressure of ammonia over the solution being investigated. Thus, loss of ammonia vapor to the gas stream during the weighings was avoided. At the conclusion of the experiment the total quantity of ammonia and the weight of cesium present were checked by analysis and found to be as expected.

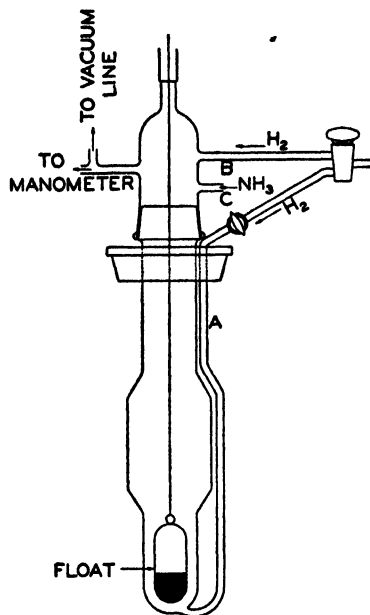


FIG. 2. *Apparatus for measuring solution densities.*

3. Electrical Conductivity

The electrical conductance of the cesium-ammonia solutions was required for comparison with the conductance data reported for sodium and potassium solutions by Kraus and Lucasse (13, 15). Also, a careful study of conductance should reveal the presence of any liquid-liquid phase separation under the conditions employed, and it was of interest to observe the change of conductance on freezing. Several types of cell were tried for these measurements, and the final design was adopted only after several facts were appreciated:

- (1) The conductance of these solutions is, like that of the other alkali metal solutions in ammonia, very high. Accordingly, the cell must be designed to give a long current path and a small conductor cross section.
- (2) The reaction of cesium with ammonia is much more rapid than that of the other alkali metals, and it is catalyzed by the presence of cesium amide. This fact precluded the use of a capillary cell and necessitated geometry that would allow bubbles of hydrogen to rise out of the current path.
- (3) The cell geometry had to allow for adequate mixing of the solution after each addition of ammonia, since the cost of cesium and the manipulative difficulties made it preferable to start with a concentrated solution and dilute it several times before renewal.

- (4) It was necessary to have a constant cross section for the current path,
- (5) The cell had to remain vacuum-tight even after freezing in liquid air and remelting. This requirement was perhaps the most difficult to fulfill.

The conductance cell is shown in Fig. 3. The tube in which the platinum electrodes are located has a capacity of about 2 ml. Since platinum sealed

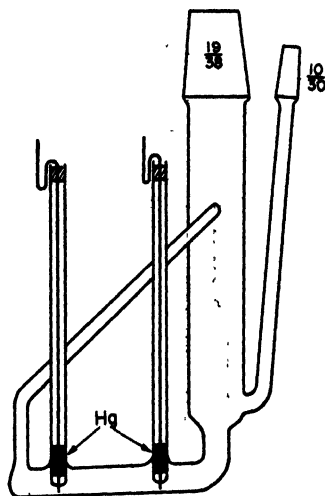


FIG. 3. Conductance cell.

through Pyrex is not vacuum-tight, mercury is used in the electrode wells. This ensured the tightness of the apparatus even when the mercury was frozen. The tube leading from the end of the electrode chamber diagonally back to the vertical tube is for stirring the solution. For this experiment, cesium metal was sealed into tubes 3 mm. in diameter. An appropriate length of one of these tubes was broken off, and introduced in the side arm on the cell. When melted *in vacuo*, the cesium ran down into the body of the cell. When fresh ammonia had been distilled into the cell, the frozen solution was melted and the cell tilted clockwise (with reference to Fig. 3); this provided adequate mixing.

The electrodes were lightly platinized and the cell constant was determined with standard potassium chloride solutions at 25° C., using Shedlovsky's figures (23). Two bridges were used for the measurement of resistance. For the dilute solutions (up to a concentration of $\text{NH}_3 : \text{Cs} = 20 : 1$), a conventional type of a-c. conductance bridge was employed, using a 1000 cycle oscillator as the source, with a Leeds and Northrup Kohlrausch slidewire for the ratio arms, and a DuMont oscilloscope as the balance detector.

The conductance of the more concentrated solutions is very high and is electronic rather than electrolytic, as demonstrated so clearly by Kraus and others (12, 15). Thus, in the range where the a-c. conductance measurements were becoming more difficult owing to capacity effects, a Leeds and Northrup

direct-current bridge having a sensitivity of better than 0.001 ohm was employed. As the current direction was reversed on each successive measurement, there was little to fear from polarization interference. A range of concentrations from 0.05 *N* to 6.7 *N* was studied at $-70 \pm 0.2^\circ \text{C}$. Conductance measurements were made too on the solutions when frozen in liquid air. The temperature of -70°C . was chosen as the experimental temperature because it was felt that a check on the possible formation of two liquid phases could thus be obtained. That is, since the electrodes are at the bottom of the cell, and if two liquid phases did form, the conductance of the tranquil solution would be different from that of the agitated solution when the two phases were intermixed. Accordingly, measurements of conductance were made at each concentration of the solution immediately after violent agitation and also after long standing. No difference in conductance was observed at any time.

To maintain the conductance cell at -70°C ., it was immersed in stirred acetone contained in a nickel beaker surrounded by "dry-ice" snow. A thermoregulator operated a heater that maintained the bath at the required temperature.

(B) EXPERIMENTAL RESULTS

1. Vapor Pressure of Cesium Solutions at -50°C .

The vapor pressure curve in Fig. 4 is drawn from the following data:

Wt. of cesium used = 3.825 gm. = 0.0287 gm-atoms of cesium.

TABLE I

Solution No.	Moles NH_3	Mole ratio $\text{NH}_3 : \text{Cs}$	V.p., mm. Hg
1	0.0505	1.76	43.5
2	0.0636	2.22	43.8
3	0.0736	2.57	44.9
4	0.0832	2.90	46.3
5	0.0891	3.11	47.6
6	0.0951	3.31	51.0
7	0.1011	3.52	56.2
8	0.1071	3.73	59.0
9	0.1130	3.94	63.8
10	0.1190	4.15	72.7
11	0.1249	4.36	80.0
12	0.1296	4.52	83.3
13	0.1309	4.56	84.9
14	0.1396	4.87	97.4
15	0.1497	5.22	113.1
16	0.1598	5.54	128.6
17	0.1699	5.92	146.9
18	0.1905	6.57	177.0
19	0.2110	7.34	203.4
20	0.2316	8.07	224.6
21	0.2653	9.24	245.7
22	0.2805	9.79	252.6
23	0.2957	10.30	257.2
24	0.2931	10.21	258.0

TABLE I—*Concluded*

Solution No.	Moles NH_3	Mole ratio $\text{NH}_3 : \text{Cs}$	V.p., mm. Hg
25	0.3032	10.56	260.0
26	0.3109	10.83	264.7
27	0.3260	11.35	268.3
28	0.3412	11.90	273.5
29	0.3564	12.41	277.0
30	0.3716	12.95	284.6
31	0.4026	14.02	282.8
32	0.4026	14.02	284.0
33	0.4177	14.55	285.8
34	0.4328	15.09	286.8
35	0.5035	17.54	291.8

The dotted curve in Fig. 4 is that of vapor pressure as a function of concentration, if the solution obeys Raoult's law. Pure ammonia has a vapor pressure at -50°C . of 310.7 mm. (5). The last point shown on the curve in

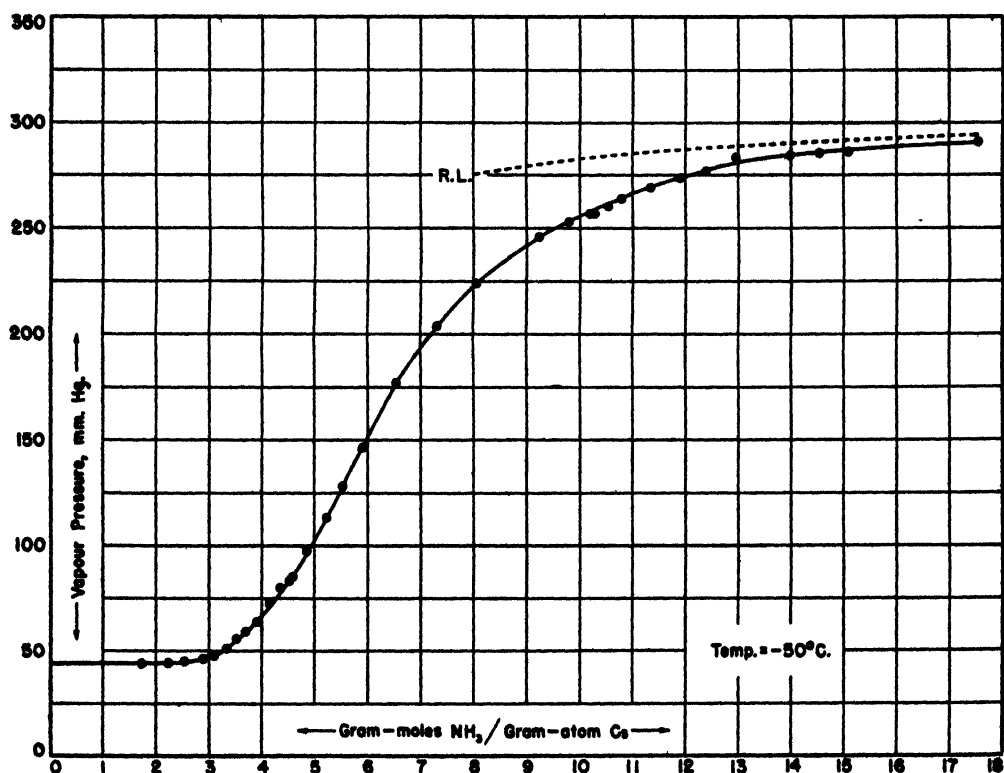


FIG. 4. Vapor pressure - concentration curve for cesium-ammonia solutions.

Fig. 4 represents a vapor pressure of 291.8 mm. for a solution of concentration about 2 *N*—a vapor pressure depression of 18.9 mm. For the same concentration of a solution that obeys Raoult's law, the vapor pressure depression

would be 16.75 mm. Accordingly, as one would expect, the deviation from Raoult's law is considerable for a 2 *N* solution; the concentration at which the solution first shows departure from Raoult's law was not determined in this experiment, since its accuracy would be low compared with that of a tensimeter measurement. For stronger solutions the atomic weight of cesium calculated on the basis of Raoult's law is markedly less than 132.91 (e.g., for point 21 on the curve the gram-atomic weight is 54.6). These observations are in agreement with those made by many workers on the vapor pressures of sodium solutions in ammonia. The increase in vapor pressure in passing from a saturated solution to those slightly less concentrated in metal is quite gradual, in contrast to that shown by the curve for sodium-ammonia solutions, in which the change is very abrupt. This probably indicates that ammonia is considerably more soluble in cesium than in sodium. The concentration of a saturated solution of cesium in ammonia at $-50^{\circ}\text{C}.$, as obtained from the vapor pressure curve, is 77.05% by weight ($\text{NH}_3 : \text{Cs}$ ratio = 2.34).

2. Density of Cesium-ammonia Solutions

The results of these experiments are expressed in the graph comprising Fig. 5, and in Table II.

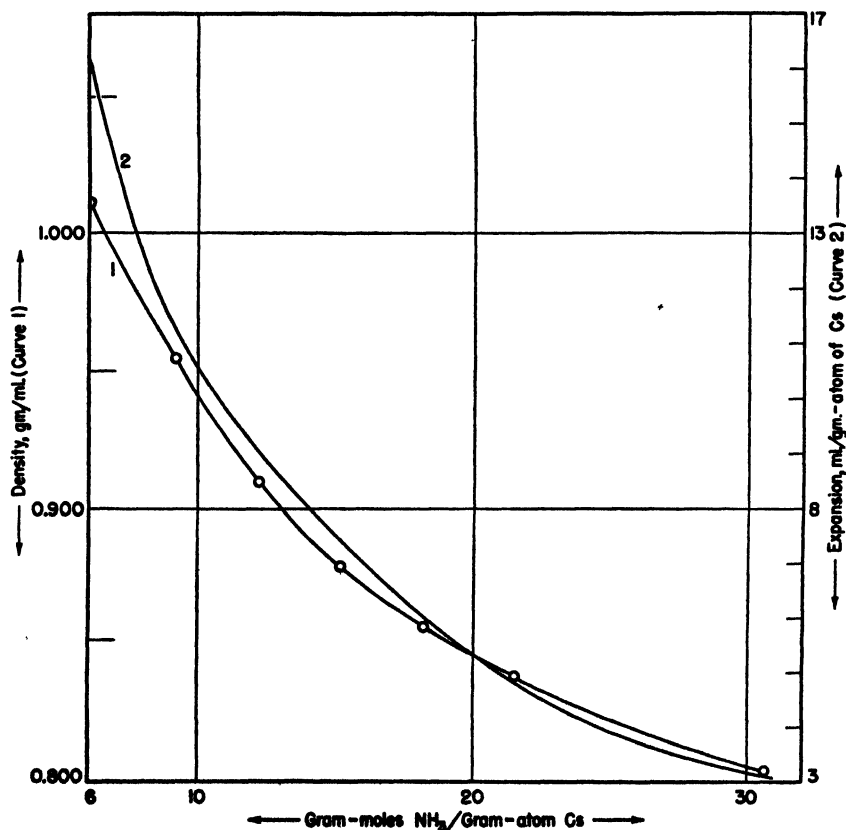


FIG. 5. Density of cesium-ammonia solutions at $-50^{\circ}\text{C}.$

TABLE II

Solution No.	Mole ratio $\text{NH}_3 : \text{Cs}$	Density, gm. per ml.	Expansion, ml. per gm-atom of Cs
1	6.12	1.0140	16.2
2	9.20	0.9545	11.0
3	12.20	0.9095	9.2
4	15.25	0.8788	7.5
5	18.19	0.8570	6.1
6	21.55	0.8392	4.7
7	30.60	0.8041	3.1

For the calculation of the expansion of the solution per gram atom of cesium, the following data were used:

Wt. of cesium used in this experiment = 2.1725 gm.

Density of metallic cesium at -50°C. = 1.927 (8, p. 35).

Density of ammonia at -50°C. = 0.7020 (4).

The maximum expansion measured was somewhat less than that recorded for sodium in ammonia (14), and the variation with concentration is much more pronounced.

3. Electrical Conductance Measurements

The values for the conductance of cesium solutions in liquid ammonia at -70°C. are given in Table III.

TABLE III

Soln. No.	Mole ratio $\text{NH}_3 : \text{Cs}$	$N^{\circ}y$	$\log V$	K	λ
6	7.88	4.00	-0.718	650.0	162,500
7	11.40	2.99	-0.558	400.0	133,000
8	14.93	2.40	-0.440	222.0	92,600
9	18.49	2.00	-0.348	89.6	44,800
10	21.98	1.72	-0.273	23.8	13,830
11	25.50	1.51	-0.208	3.12	2070
12	28.96	1.35	-0.150	1.36	993
13	32.50	1.21	-0.102	0.81	670
14	36.0	1.10	-0.059	0.63	572
16	55.2	0.74	0.127	0.332	449
17	111.1	0.38	0.434	0.133	354
18	159.5	0.26	0.589	0.084	318
21	980.0	0.04	1.377	0.016	381

In the above table, V , the dilution, is the number of liters of solvent containing 1 gm-atom of solute, K is the specific conductance, and λ is the equivalent conductance. The conductance of the concentrated solutions, as one would expect, varies enormously with concentration. At a concentration of about 0.2 N , the equivalent conductance passes through a minimum of about 300 reciprocal ohms. The most concentrated solution measured, 4 N ,

has a specific conductance of 650 reciprocal ohms, or about 1/16 that of metallic mercury. If comparison is made of these results with those for sodium-ammonia solutions, some care must be exercised because of an error in calculation made by C. A. Kraus (13, p. 761), which has been quoted in subsequent

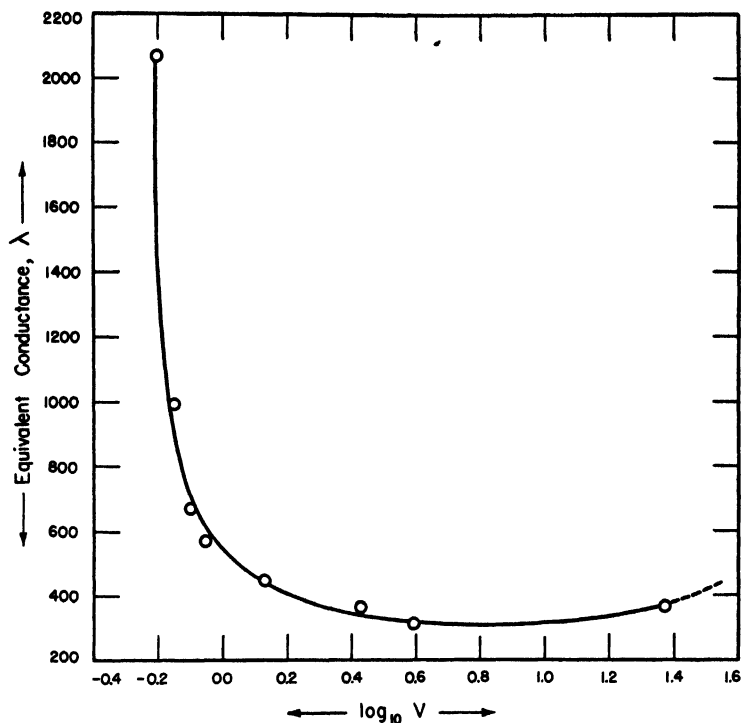


FIG. 6. *Electrical conductance of cesium-ammonia solutions at -70°C .*

literature (11). The statement cited from his paper that the specific conductance of a 2 *N* solution of sodium in ammonia is 1/6 that of metallic mercury is in error, since the conductance figures show that the factor should be 1/60.

The values of the conductance of cesium-ammonia solutions at -70°C . have the order of magnitude that one would predict for them on the basis of the temperature coefficients derived by Kraus (13) for sodium solutions.

No evidence was found in all the work done with the cesium-ammonia solutions of any formation of two liquid phases down to -70°C . The conductances were investigated over a concentration range of 0.04 to 7 *N* and in no instance was there any change in the conductance at -70°C . on agitation of the solution in the cell. It has therefore been concluded that the cesium-ammonia solutions do not undergo the liquid-liquid phase separation in the concentration and temperature regions noted.

Since no region of liquid phase separation has been established, an arbitrarily chosen solution of 0.49 *M* ($\text{NH}_3 : \text{Cs} = 82.5$) was investigated for superconducting properties at liquid nitrogen temperatures. The apparatus used

was that described in a previous publication (10). No positive results were obtained with 20 trials on this solution. Since Ogg's theory (20) has as a prerequisite, the formation of two liquid phases, these measurements were not extended.

The resistance of the cesium solutions, like that of the sodium solutions, plunges downward as the solutions are cooled in liquid air. A sample of 0.302 *M* was slowly frozen at -78°C . The resistance rose in three minutes (starting at -70°C .) from 140 ohms to 369 ohms, and then fell by the end of 10 min. to a value of 3 ohms. In liquid air, the resistance was 0.4 ohm. This behavior is similar to that observed by Birch and MacDonald for sodium solutions (1), and is also doubtless due to the formation of a eutectic, since the solid at liquid air temperature is silver colored, like the sodium solutions, and unlike the frozen lithium solution, which is bronze in color.

Discussion

1. The vapor pressure curve indicates that the departure from Raoult's law is similar to that shown by sodium solutions. The solubility at -50°C . is 77.05% by weight.

2. The solutions show an expansion at -50°C . of 16.2 ml. per gm-atom of cesium for a $\text{NH}_3 : \text{Cs}$ concentration of 6.1, falling off to a value of 3.1 for $\text{NH}_3 : \text{Cs}$ of 30.6.

3. The conductance of the cesium solutions at -70°C . goes through a minimum at a concentration of 0.2 *N*. In magnitude, the conductance of the concentrated solutions approaches that of metals.

4. There is no separation into two liquid phases down to -70°C . for solutions between 0.04 *N* and 7 *N*.

As mentioned in the introduction, this investigation was carried out as a sequel to an earlier one in which some indication of persistent currents was observed in certain solutions of sodium in ammonia when frozen in liquid air. Since there was no similar phenomenon in the cesium solutions used, the work has now been discontinued. It now appears unlikely that the persistence of these currents in the sodium solutions is attributable to the superconducting state; a short discussion of this point is now under preparation.

Acknowledgment

The author is glad of this opportunity to acknowledge his indebtedness to Dr. E. A. Flood of the National Research Council for his advice and assistance in this investigation. Most of the above work was performed in Dr. Flood's laboratory and this is an opportune time to express thanks to the Chemistry Division of the National Research Council of Canada for this and for many other courtesies extended during the past several years.

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SOME NOTES ON THE PROPERTIES OF METAL-AMMONIA SOLUTIONS¹

By J. W. HODGINS AND E. A. FLOOD

Abstract

Some experiments are described that corroborate earlier observations of minute persistent currents in frozen rings of solutions of sodium in ammonia. It is shown, however, that it is unlikely that these currents are due either to superconductivity of the solid or to orientation of crystals in the magnetic field. Comment is made on the presence of two liquid phases in lithium-ammonia solutions.

I. Persistent Current Measurements

In 1946, the author published (6) what was to be the only corroboration of some observations by R. A. Ogg, Jr. (8) of the persistence of currents induced in certain frozen solutions of sodium in liquid ammonia. Numerous other investigators have reported negative results for the same experiments (2, 3, 5); Gibney and Pearson (4), on the basis of the low values that they obtained for the magnetic susceptibility, discredit the postulate that the frozen solid is superconducting.

In the face of such adverse opinion, it was thought advisable to repeat the experiments for the detection of persistent currents induced in frozen rings of solution. The same apparatus was used as was described in (6), but some changes were made in the technique. Liquid nitrogen was used as the refrigerant to avoid the possible interference from paramagnetic oxygen. Also the sequence of operation was as follows:

1. The ring of liquid solution at -40°C . (mole ratio $\text{NH}_3 : \text{Na} = 25 : 1$) was suspended in the center of a solenoid producing a magnetic flux of 1600 gauss.
2. The ring of solution was carefully frozen by immersion in liquid nitrogen.
3. After two minutes, the nitrogen was removed and a search coil immediately placed under the frozen ring (the search coil was out of circuit at this stage).
4. The magnetic field was shut off, causing the flux to decay through the horizontal ring, and the search coil was connected to a galvanometer about $1/10$ second later.
5. Any deflection of the galvanometer must be due to a change in the magnetic field about the search coil caused by a persistent current in the ring of solution.

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Contribution from Defence Research Chemical Laboratories, Ottawa, and the National Research Laboratories, Ottawa. Issued as DRCL No. 31 and as N.R.C. No. 2041.

6. Unless a galvanometer deflection was obtained, the solution was remelted in liquid ammonia after each observation and the procedure repeated. When a deflection was noted, however, the frozen ring was not allowed to melt but after the indications of current had disappeared the procedure was repeated with the magnetic flux in the reversed direction. Thus, if the ring were superconducting, the second deflection should be in the reverse direction.
7. Finally, the experiments were carried out in the magnetically quiet period of the day (1 to 6.30 a.m. in Ottawa) on a table on which all the apparatus was earthed to dissipate electrostatic charges. The sensitivity of the apparatus was such that 1 mm. galvanometer deflection corresponds to 8 ma. in a single turn of conductor. This denotes a change in field of 2×10^{-3} gauss.

Out of 40 trials made, only 5 galvanometer deflections were observed. The largest of these corresponded to 32 ma. of current in the ring of solution and lasted for less than 20 sec. However, the direction of this "persistent current" did not change with the direction of the magnetic field as it should if the ring were superconducting. And yet no rapid galvanometer deflections of this magnitude had been observed when the magnetic field in the room was monitored over long periods with the search coil.

If the currents observed were due not to the superconducting property of the frozen solution, but were caused by the occasional preferred orientation of charge by the action of the magnetic field on crystals in the frozen solution, then the fact that the solution was in the form of a ring would be of no importance. To check this point the experiments were repeated on a solution (mole ratio $\text{NH}_3 : \text{Na} = 25 : 1$) in the form of a bar with an electrode at each end. The solution was frozen in the magnetic field as before and the field discontinued after two minutes' refrigeration in liquid nitrogen. About 1/10 sec. later a galvanometer was connected between the electrodes. Forty such experiments yielded negative results.

Accordingly, the following conclusions must be drawn:

- (a) It is unlikely that solutions of sodium in ammonia (concentration about 1 *N*) are superconductors when frozen in liquid nitrogen.
- (b) The sporadic currents observed are not due to magnetically oriented charged crystals in the frozen solution.

All the other "ring" experiments reported (including those of Ogg himself) were carried out with the solution in contact with the atmosphere. This introduces so many additional variables that it is no longer proper to refer to the system as sodium-ammonia, since there will be contamination by oxide, hydroxide, and ice, not to mention the uncertainty of composition. Accordingly it is felt that while other investigators reached the same conclusions as above, the inferences drawn were not completely justified by their means of attainment.

II. Liquid-liquid Phase Separation in Lithium and Cesium Solutions in Ammonia

Birch and MacDonald (1, p. 737) state, "It can be concluded that liquid-liquid phase separation above -78°C . is exhibited by all except lithium, although a slight doubt exists in the case of potassium."

In the preceding publication the author found no evidence of liquid-liquid phase separation with cesium solutions down to -70°C . in the concentration range from $0.050\text{ }N$ to $7\text{ }N$. Also, there is no doubt that lithium solutions do separate into two liquid phases above -78°C . This was pointed out first by Kraus and Johnson (7), who observed a flat portion in the vapor pressure curve at -39.4°C . between the concentration $\text{NH}_3 : \text{Li} = 25$ and $\text{NH}_3 : \text{Li} = 45$ (mole ratios).

To check this point a solution of mole ratio $\text{NH}_3 : \text{Li} = 15.5 : 1$ was made up in a conductance cell with tiny platinum electrodes at the bottom of a trough running across the cell. The resistance of the solution was measured at a series of temperatures between -38°C . and -70°C . The solution was allowed to stand 10 min. at each temperature before the resistance was determined. A sharp increase in resistance occurred at about -60°C .; this indicated the formation of a second liquid phase. And indeed, at -70°C . the two phases were clearly visible, the characteristic bronze layer surmounting the deep blue solution.

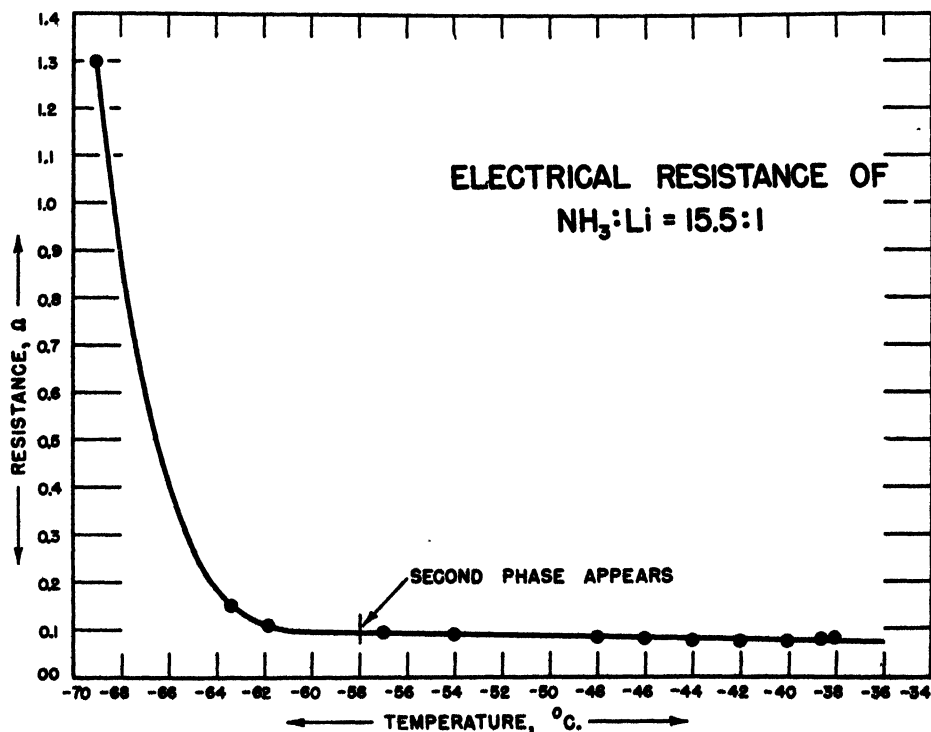


FIG. 1

Thus the statement of Birch and MacDonald should be amended to read, "Liquid-liquid phase separation above -78°C . is exhibited by all except cesium. . . ."

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THE SORPTION OF ACIDS BY WOOL¹

BY R. DONOVAN AND P. LAROSE¹

Abstract

The amount of acid sorbed by wool from solutions of sulphuric acid of four different strengths (namely, 0.0505, 0.0339, 0.0182, and 0.0101 molar) and containing sodium sulphate in amounts varying up to 0.16 molar has been determined. It has been found that the presence of the salt has little effect on the quantity of acid sorbed within those limits. The results are analyzed in the light of the theory of Gilbert and Rideal but this theory fails to give a satisfactory explanation of the results obtained. It is possible, however, to explain the results of the authors' experiments on the basis of the recent application of the Donnan equilibrium by Peters and Speakman. The Langmuir adsorption isotherm equation has been applied to data on the absorption of hydrochloric acid and of sulphuric acid by wool. The data appear to fit the Langmuir equation and give, for the maximum combining capacity, values that agree well with those estimated in other ways.

Introduction

The sorption of acids by wool has been studied by a number of investigators and most of the evidence points to a chemical combination between the wool and the acid. Various theories have been advanced to explain the mechanism of acid sorption by wool, but none can be said to be entirely satisfactory from a quantitative point of view, the agreement between theory and experimental results being limited in most cases to a narrow range of the data. However, as this paper was under preparation, Peters and Speakman (12) published a paper in which the Donnan equilibrium is applied with some success to explain the sorption of hydrochloric acid and of sulphuric acid. Elöd (2) and Elöd and Silva (3) have also applied the Donnan equilibrium concept to the sorption of acids by wool, but the agreement between the experimental and the calculated results was only qualitative. The early results of Georgievics (6, 7), Fort and Lloyd (4), Paddon (11), Wilkinson and Tyler (21), and others do not lend themselves to proper quantitative interpretation, since the conditions under which the experiments were carried out were not such as to ensure equilibrium, or the data reported are not sufficiently complete. Harris and coworkers (20) and Steinhardt (18, 19) have used the various dissociation constants of the protein-acid complex to explain the results they obtained with a number of acids. To account for the high sorption of certain weak acids, they postulated direct combination of undissociated acid molecules with the wool.

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Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1962.

Gilbert and Rideal (9) extended to the adsorption of ions on wool an expression given by Fowler and Guggenheim (5, p. 426) for the adsorption of molecules on definite sites of the absorbent. Their theory was successful to some extent when applied to the results of Steinhardt and Harris (17) and to those of Speakman and Stott (16). Gilbert (8) applied the theory to the results obtained by Speakman and Clegg (15) in determining the effect of sodium sulphate concentration on the absorption of a number of acid dyes by wool.

It was evident from a review of the previous work on the subject that further experimental data was required before a general theory could be deduced to explain the acid sorption by wool. With this in mind, the authors decided to study the effect of sodium sulphate on the sorption of sulphuric acid by wool. Although the sorption of the acid itself has been studied, no systematic study seems to have been made of the action of sodium sulphate on the acid sorption. The effect of sodium sulphate on the sorption of the dye Orange II was also studied, but this will form the subject of another paper.

Experimental Procedure

The wool used in our experiments was in the form of a fine worsted yarn that had received no bleaching or other chemical treatment except the usual scouring applied during manufacture. No special purification treatment was given to the wool but it was equilibrated to a pH of 5.7 to 5.8 before the tests by soaking it in a weak acetic acid bath of pH 4.5 until the pH was about 5.1 to 5.2 and then soaking it overnight in distilled water, which brought the pH up to 5.7 to 5.8. The ash in the wool was negligible after this treatment but the wool contained a small percentage ($\sim 1\%$) of fatty and waxy material for which no correction was made. The wool was not dried prior to testing but it was conditioned in a standard atmosphere of 65% R.H. and $21^{\circ}\text{C}.$, and a control sample was used to determine the moisture content so that the appropriate correction could be made to the samples to convert all results to a dry wool basis.

Samples weighing 2.5 gm. (dry weight) were placed in flasks containing 250 ml. of the solution with known amounts of acid and sodium sulphate. The wool was thoroughly wetted with distilled water and wrung before immersion. Correction for the water adhering to the wool was made by weighing the flask with the wool and solution to determine the exact amount of solution. The flasks were allowed to stand for 64 hr. in a bath maintained at $30^{\circ}\text{C}.$ Aliquot portions of the solution were then removed for determination of acid and sulphate contents. The difference between the initial and final concentrations was taken as a measure of the sorption. pH determinations were also carried out on the solutions before and after the tests, by means of a model G Beckman pH meter calibrated at a pH of 4.00 with 0.05 *M* potassium acid phthalate. The acid strength was determined by titration with a standard sodium hydroxide solution and phenolphthalein indicator. The sulphate content was determined gravimetrically by precipitation as barium sulphate.

Results

Table I summarizes the results obtained.

TABLE I

AMOUNT OF ACID SORBED BY WOOL FROM SULPHURIC ACID SOLUTIONS
WITH DIFFERENT AMOUNTS OF SODIUM SULPHATE

Na ₂ SO ₄ , moles/liter	pH		Acid sorbed, millimoles/gm.	SO ₄ sorbed, millimoles/gm.
	Before	After		
Original concentration of acid = 0.0505 mole/liter				
0.16	1.55	1.60	0.455	0.356
0.08	1.39	1.45	0.474	0.381
0.04	1.33	1.36	0.396	—
0.02	1.34	1.31	0.448	0.409
0.016	1.24	1.29	0.451	0.430
0.008	1.24	1.27	0.442	0.472
0.004	1.22	1.26	0.402	0.371
0.0008	1.23	1.24	0.419	0.477
0.0000	1.19	1.24	0.452	0.466
Mean			0.438	0.420
Original concentration of acid = 0.0339 mole/liter				
0.16	1.71	1.77	0.409	—
0.08	1.60	1.65	0.427	0.423
0.04	1.48	1.52	0.456	0.422
0.02	1.42	1.46	0.441	0.410
0.016	1.38	1.44	0.443	—
0.008	1.34	1.42	0.424	0.444
0.004	1.36	1.40	0.428	0.386
0.0008	1.34	1.39	0.427	0.451
0.0000	1.32	1.38	0.433	0.435
Mean			0.432	0.424
Original concentration of acid = 0.0182 mole/liter				
0.16	2.06	2.18	0.410	0.331
0.08	1.91	2.01	0.396	—
0.04	1.82	1.91	0.397	0.321
0.02	1.72	1.83	0.427	—
0.016	1.71	1.82	0.398	0.376
0.008	1.69	1.77	0.403	0.420
0.004	1.65	1.75	0.397	0.403
0.0008	1.56	1.67	0.407	0.397
0.00	1.62	1.72	0.389	0.398
Mean			0.403	0.378
Original concentration of acid = 0.0101 mole/liter				
0.04	2.14	2.29	0.378	0.374
0.02	2.00	2.19	0.365	0.362
0.008	1.83	2.03	0.379	0.367
0.004	1.89	2.08	0.364	0.356
0.0008	1.85	2.02	0.365	0.360
0.00	1.83	1.98	0.357	0.357
Mean			0.368	0.363

NOTE: All calculations are based on the weight of dry wool.

Discussion

The results will be examined in the light of the Donnan equilibrium as recently applied by Peters and Speakman (12) and according to the concept introduced by Gilbert and Rideal (9) but before this is done it will be well to refer to the variations noted in the results for any one strength of acid. It will be seen that there is no regularity in the figures obtained for the amount of acid sorbed as the quantity of salt is varied. The differences noted can be readily ascribed to experimental error. With the strengths of acid used, one is working close to the saturation point for wool and the amount of acid sorbed is obtained from the difference of two comparatively large quantities so that any error in the actual strength determination is magnified several times when applied to the amount sorbed. This is emphasized by the observation that the variation in the results becomes less as the acid becomes weaker. The same remarks apply even more to the sulphate determinations, particularly where the salt concentration is high. For example, it has been estimated that the error in the calculated amount of sulphate sorbed from the 0.0505 molar acid containing salt of 0.16 molar concentration is a hundred times the error in the determination of the sulphate in the test solution.

For this reason, the authors do not consider significant the differences between the amount of acid sorbed as determined by change of acidity and the change in sulphate concentration. The acid sorbed is also considered constant for any one strength of acid irrespective of the salt concentration.

The results obtained with the acid solutions without salt are in fair agreement with those reported by Speakman and Stott (16), as Table II shows.

TABLE II

MILLIMOLES OF SULPHURIC ACID SORBED PER GRAM OF DRY WOOL FOR DIFFERENT pH VALUES

pH	Speakman and Stott	Authors' results	
		Acid alone	Acid + salt (Mean)
1.24	0.45	0.45	0.44
1.38	0.44	0.43	0.43
1.72	0.41	0.39	0.40
1.98	0.38	0.36	0.37

Gilbert and Rideal Theory

Gilbert and Rideal (9) in applying their theory to the sorption of sulphuric acid assumed complete dissociation of the acid. Sulphuric acid, however, even in moderately dilute solutions, contains an appreciable proportion of hydrosulphate ions, and for solutions of low pH values this cannot be disregarded, particularly in the presence of sulphates, which increase the sulphate ion concentration of the solution and therefore depress the dissociation of the

hydrosulphate ion. Following the reasoning of Gilbert and Rideal but taking into consideration the hydrosulphate ions, we obtain this expression:

$$\ln \frac{\theta_H}{1 - \theta_H} \cdot \frac{\theta_{SO_4}}{\theta_{HSO_4}} = \ln \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} - \frac{\Delta\mu_H + \Delta\mu_{SO_4} - \Delta\mu_{HSO_4}}{RT} \quad (1)$$

Both terms on the right hand side are constant, so we may write

$$\frac{\theta_H}{1 - \theta_H} = K \frac{\theta_{HSO_4}}{\theta_{SO_4}}, \quad (2)$$

where K is a constant involving the dissociation constant of the hydrosulphate ion and the affinities of the various ions for wool. However, we have no means of measuring θ_{HSO_4} and θ_{SO_4} separately, the total only being known. Consequently the validity of Equation (1) or Equation (2) cannot be determined readily by experiment. In order to simplify the problem, one could assume that the hydrosulphate ion has a much higher affinity for wool than the sulphate ion and is therefore taken up in preference, or vice versa. If such were the case, the Gilbert and Rideal theory predicts a straight line relation between pH and the logarithm of the anion concentration when θ_H is constant, but our results fail to show such a relation, when a value of 0.88 milliequivalent of acid per gram of wool is taken for the maximum absorption capacity of the wool. It should be pointed out that agreement of the results with the Gilbert and Rideal (9) theory depends to some extent on the choice of this maximum value, but the same lack of agreement was obtained with any reasonable value for the absorption capacity of wool.

As one of the objections to the Gilbert and Rideal theory, Peters and Speakman (12) cite the lack of linear relation between $\log \frac{\theta}{1 - \theta}$ and pH. This objection, based apparently on a value of 0.82 milliequivalent per gram for the combining capacity of wool, is not valid, since Fig. 1 shows that it is possible to obtain a straight line when another value is chosen for the combining capacity. The data of Steinhardt and Harris (17) for hydrochloric acid have been redrawn, with values of 0.90 m.e. (milliequivalent) and 0.82 m.e. for the saturation point. It will be seen that the experimental points lie closely on a straight line when the value of 0.90 is chosen. The objection to the theory of Gilbert and Rideal (9) is rather that it predicts a slope different from that found. A slope of 1 is predicted in this case, whereas the slope of the line in Fig. 1 is 0.80. Use of the activity coefficients would have little effect on this slope.

In an attempt to obtain an independent and convenient way to determine the saturation point for wool, we have applied the Langmuir equation for the adsorption isotherm in the form

$$\frac{c}{x} = \frac{1}{x_m b} + \frac{c}{x_m}$$

where x is the amount of acid sorbed,

x_m is the maximum amount that wool can take up,

c is the concentration of acid in the solution, and

b is a constant dependent on temperature.

Plotting c/x against c gives a straight line with a slope $1/x_m$, from which x_m is determined.

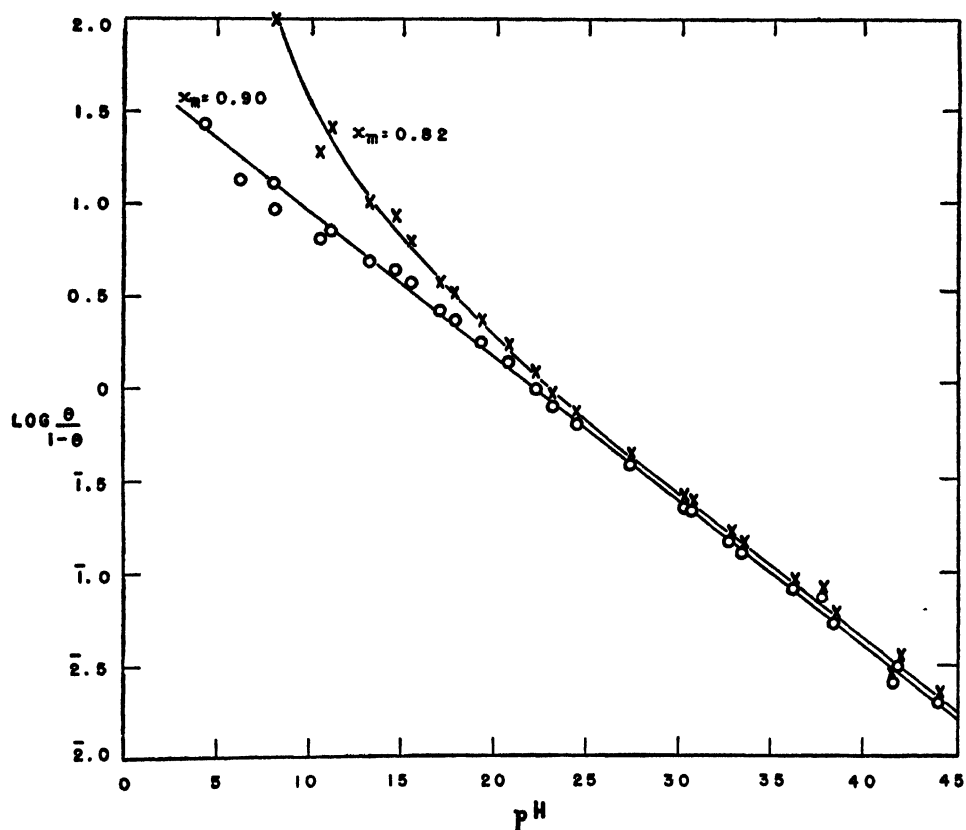


FIG. 1. Results of Steinhardt and Harris (17) for hydrochloric acid sorbed by wool, plotted as a test of the Gilbert and Rideal theory (9). x_m = maximum capacity of wool in milliequivalents per gram.

It should be remembered that the Langmuir equation can be derived from statistical considerations and that it leads to an equation of the same form as that derived by Gilbert and Rideal for acid sorption without salt. The results of Steinhardt and Harris (17) for hydrochloric acid have been plotted according to the Langmuir equation given above in Fig. 2, which gives a slope of 1.17 or $x_m = 0.854$ m.e. per gram of wool. The data of Speakman and Stott (16) for sulphuric acid plotted in Fig. 3 give a slope of 1.14 or $x_m = 0.876$ m.e. per gram. This is the same as the limiting combining capacity found by Peters and Speakman (12) for hydrochloric acid [Case (ii) in their paper]. It may be mentioned also that Lemin and Vickerstaff (10) in their calculations of the affinity of monobasic dyes for wool used a value

of 0.90 milliequivalent per gram for the limiting combining capacity of wool. They found that this represented closely the capacity of wool for the dyes they investigated. There seems to be little doubt then that the figure of

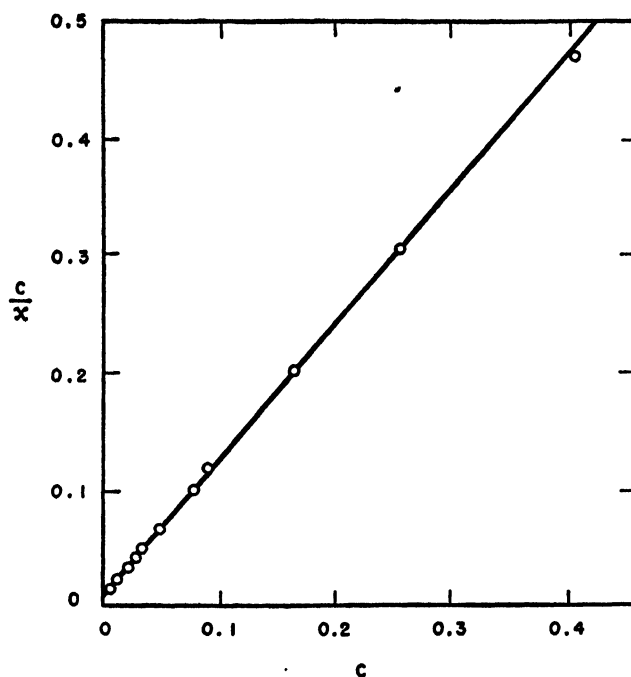


FIG. 2. Results of Steinhardt and Harris (17) for hydrochloric acid sorbed by wool, plotted according to the Langmuir equation.

c = concentration of acid in the solution.

x = amount of acid sorbed.

0.82 m.e. per gram assumed by many investigators to represent the limiting capacity of wool for acids is too low. Speakman and Stott have found a higher apparent combining capacity for sulphuric acid and other acids such as oxalic and phosphoric, but in a recent paper Peters and Speakman have succeeded in explaining this, in the case of sulphuric acid at least, by application of the Donnan equilibrium concept.

Donnan Equilibrium, as Applied by Peters and Speakman

We have followed Peters and Speakman's treatment (12) in applying the Donnan equilibrium to our results, but without neglecting the presence of hydrosulphate ions. We have also attempted to correct for the activity of the sulphate ions.

In order to simplify the calculation of sulphate and hydrosulphate ion concentration we have made the assumption that the activities of the hydrogen ion and of the hydrosulphate ion are the same in the expression

$$\frac{[H^+] \gamma_H [SO_4^{2-}] \gamma_{SO_4}}{[HSO_4^-] \gamma_{HSO_4}} = K = 0.012, \quad (3)$$

where γ is the activity coefficient of the ion designated by the subscript. It is unlikely that the ratio γ_H/γ_{HSO_4} is 1 but in view of the low value of γ_{SO_4} , the error introduced by this assumption is probably small. To obtain γ_{SO_4} we

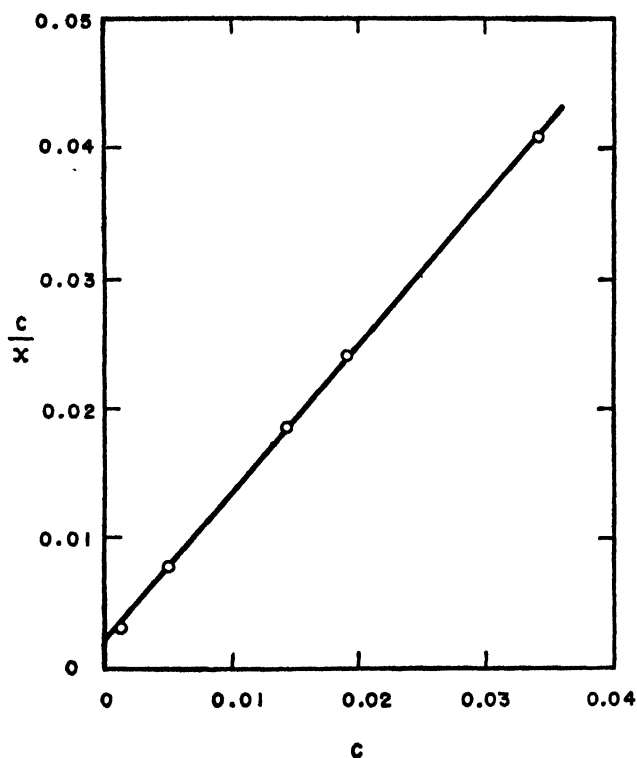


FIG. 3. Results of Speakman and Stott for sulphuric acid sorbed by wool, plotted according to the Langmuir equation.

c = concentration of acid in solution.

x = amount of acid sorbed.

have followed the practice of Shrawder and Cowperthwaite (14) of taking the value of $\gamma \pm$ for bi-bivalent sulphates and we used the values given by Cowperthwaite and LaMer (1) for zinc sulphate. In order to estimate the SO_4 concentration introduced by the addition of sodium sulphate, it was also necessary to make a correction for the incomplete dissociation of the salt. To do this, we have used the values of Righellato and Davies (13) for the degree of dissociation of the $NaHSO_4$ ion.

Having obtained the concentrations of HSO_4 and SO_4 ions from Equation (3) we substituted these in Equation (4), given by Peters and Speakman (12),

$$\frac{a}{2v} = \left(\frac{\lambda^2}{\gamma_2} - 1 \right) [SO_4^{2-}] + \left(\frac{\lambda}{\gamma_1} - 1 \right) [HSO_4^-], \quad (4)$$

using their notation, where

a = amount of acid combined in the wool,

v = volume of the internal phase,

$$\lambda = \frac{H\gamma_H}{h\gamma_h} \left(\frac{w}{W} \right)^{r_H},$$

$$\gamma_2 = \frac{\gamma_{\text{SO}_4}}{\gamma_{\text{SO}_4}} \left(\frac{W}{w} \right)^{r_{\text{SO}_4}},$$

$$\gamma_1 = \frac{\gamma_{\text{HSO}_4}}{\gamma_{\text{HSO}_4}} \left(\frac{W}{w} \right)^{r_{\text{HSO}_4}},$$

γ is the activity coefficient of the ion designated by the subscript,
 r is the ratio of the partial molar volume of the ion to that of water,
 w and W are the activities of the water in the internal and external phases respectively, small letters being used to denote quantities in the internal phase and capital letters for the external phase.

The values of v taken are those given by Peters and Speakman for sulphuric acid at corresponding pH. This supposes that the effect of salt addition on the swelling of wool is negligible within the range of concentrations studied. This is perhaps not so, but in the absence of data on the swelling of wool in sulphuric acid solutions containing sodium sulphate, this assumption had to be made. Moreover calculations of the excess of diffusible ions inside the protein over those in the external phase indicate that on the basis of the Procter-Wilson theory of swelling, the effect of salt addition would be expected to be small within the range of concentrations used in our experiments.

γ_1 was assumed to be unity. The ionic strength in the wool phase is different from that in the external phase and one would expect, therefore, the activity coefficient of the ions to be different. It was deemed unnecessary to make the correction, in the case of the monovalent ions, since the concentrations are relatively small and the activity coefficient high, but the concentration of the sulphate ion is comparatively large, being of the order of 1.2 to 1.4 M in the wool phase. Its activity is therefore lower in the wool phase and the ratio

$$\gamma_2 = \frac{\gamma_{\text{SO}_4}}{\gamma_{\text{SO}_4}} \left(\frac{W}{w} \right)^{r_{\text{SO}_4}}$$

must be quite different from one. In calculating γ_2 , it was assumed that the activity of the sulphate ion varies in the same way with ionic strength in the internal phase as it does in the external phase, and the same data were used as in the application of Equation (3) to calculate the concentration of the ions. We have no knowledge of the relative values of w and W , but we have no reasons for believing that the activity of the water is very different in the wool phase from that in the external solution, and $\left(\frac{W}{w} \right)^{r_{\text{SO}_4}}$ was assumed equal to 1. The values of λ and $vA\theta$ obtained in this way, together with the pH values of the external solution and those calculated for the internal phase, are given in Table III. The results obtained for the solutions with intermediate salt concentrations are omitted as they do not show any behavior different from that of the other salt solutions. When the activity coefficient

TABLE III
VALUES OF pH_i AND $vA\theta$ CORRECTED FOR THE ACTIVITY OF SO_4^{2-} ION

Sodium sulphate conc'n. moles/liter	λ	pH_0	pH_i	$vA\theta$
<i>Final acid concentration, 0.0461 M acid</i>				
0.00	3.64	1.24	1.80	0.852
0.02	3.14	1.31	1.81	0.848
0.04	2.88	1.36	1.82	0.844
0.08	2.48	1.45	1.84	0.844
0.16	2.13	1.60	1.93	0.844
<i>Final acid concentration, 0.0296 M acid</i>				
0.00	3.96	1.38	1.98	0.854
0.02	3.23	1.46	1.97	0.852
0.04	2.82	1.52	1.97	0.848
0.08	2.40	1.65	2.03	0.846
0.16	2.08	1.77	2.09	0.846
<i>Final acid concentration, 0.0142 M acid</i>				
0.00	4.53	1.71	2.37	0.804
0.02	3.28	1.83	2.35	0.800
0.04	2.80	1.92	2.37	0.798
0.08	2.40	2.01	2.39	0.798
0.16	2.05	2.18	2.49	0.798
<i>Final acid concentration, 0.00642 M acid</i>				
0.00	5.44	1.98	2.72	0.732
0.02	3.31	2.19	2.71	0.730
0.04	2.71	2.29	2.72	0.728
0.00*	5.36	1.98	2.71	0.765

* Peters and Speakman data.

pH_0 = pH of external solution,

$vA\theta$ = true amount of combined acid,

pH_i = pH of internal phase,

v = volume of internal phase,

A = maximum combining capacity of wool expressed as a concentration,

θ = fraction of such capacity that has been satisfied through the combination of $RCOO^-$ and H^+ ions.

of the sulphate ion is not taken into consideration, the values of pH_i are higher and the amount of acid combined lower.

Table III indicates that the saturation value for acid absorption is 0.85 to 0.86 m.e. per gram, which agrees very well with the figures given by Peters and Speakman (12) although their saturation value was obtained at a lower pH.

In order to determine the effect of the sulphate ion activity on the results given by Peters and Speakman, we have used their data for an external pH of 1.98, since this is the only point that did not require interpolation to compare with our data. The values obtained for λ , pH_i , and $\nu A\theta$ are given in the last line of Table III. The value of combined acid obtained differs little from the value of 0.757 m.e. per gm. given by the above authors but differs appreciably from our value of 0.732 for an acid of 0.00642 *M*. However Peters and Speakman give the concentration of their acid as 0.00705 *M*. The difference corresponds to 0.04 pH difference, and, from our results, this might be expected to raise the acid combined from 0.732 to 0.742 m.e. per gm.

The agreement between the value of 0.757 given by Peters and Speakman and our calculated value of 0.765 is perhaps due to the fact that the error arising from the neglect of the sulphate ion activity coefficient in calculating the concentrations of the ions in the solution cancels the error that results from neglecting the activity in calculating the concentration in the internal phase.

It would appear from these results that although the explanation given by Peters and Speakman explains satisfactorily the experimental observations, a more rigorous test of the theory is desirable by means of experiments in which the concentration of the ions, the amount of acid combined, and the degree of swelling of the wool are determined more accurately. More should also be known of the activities of the ions, particularly in the wool phase. Experiments are being planned to fill this need.

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THE REDUCTION OF CERTAIN CHLORONITROBENZENES BY DEXTROSE AND BY SODIUM ARSENITE¹

BY ROGER GAUDRY AND KARL F. KEIRSTEAD

Abstract

The reduction of seven chloronitrobenzenes to azoxy compounds by alkaline solutions of two different reducing agents, dextrose and sodium arsenite, has been studied. These two reducing agents were found to produce a better yield and a purer product than many other reducing agents. Two azoxy compounds have been prepared for the first time: 2,2'-dimethyl-3,3'-dichloroazoxybenzene and 2,2'-dimethoxy-5,5'-dichloroazoxybenzene.

Introduction

The reduction of nitrobenzene to azoxybenzene was first carried out in 1841 by Zinin (see (1)) who used alcoholic potassium hydroxide. Since that time nitrobenzene compounds have been reduced to azoxy and related compounds most frequently by the use of either alcoholic potassium hydroxide or by sodium alcoholate in alcohol solution. The applicability of these reducing agents is however limited by such factors as poor yields, impure products, or violent reactions.

The present investigation was undertaken primarily to study the general applicability of two reducing agents, sodium arsenite and dextrose, to the preparation of azoxy compounds. The use of dextrose in alkaline solution for the reduction of nitrobenzene compounds has been reported for the preparation of azoxybenzene (13) and 2,2'-dichloroazoxybenzene (9). Sodium arsenite as a reducing agent for the preparation of azoxybenzene was first used by Loesner (11). The successful application of sodium arsenite for the preparation of azoxy derivatives (2, 3) suggests that this reducing agent may have many advantages.

We found that dextrose gave better yields than sodium arsenite in the following cases: 2-chloronitrobenzene, 2,5-dichloronitrobenzene, 2-methyl-3-chloronitrobenzene, and 2-methoxy-5-chloronitrobenzene—all of which have a substituent in the ortho position. The experimental conditions and results are shown in Tables I, II, and III.

By using dextrose we obtained a 27% yield of 2,2'-dichloroazoxybenzene as compared with a yield of 11% obtained by the use of sodium arsenite. The low yield in the latter reduction may partly be explained by the results of Dains and Kenyon (6), who showed that in the reduction of 2-chloronitrobenzene by sodium methylate 7.25% of the chlorine is removed; 12.72% of the chlorine is removed in the reduction of 4-chloronitrobenzene, while no removal is observed in the reduction of 3-chloronitrobenzene under similar conditions.

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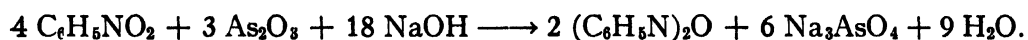
Contribution from the Department of Biochemistry, Faculty of Medicine, Laval University, Quebec. This paper constitutes part of a thesis submitted by Karl F. Keirstead to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

We found that at the end of the reaction the solution containing the dextrose-chloronitrobenzene mixture gave a white precipitate on the addition of silver nitrate. The low yields produced then by both sodium arsenite and dextrose on 2-chloronitrobenzene and 4-chloronitrobenzene are due, in part, at least, to the tendency of the chlorine in the ortho and para positions to a nitro group to be removed in the presence of a reducing agent in strong basic solution.

However, the loss of chlorine is not sufficient to explain entirely the low yields in the reactions just mentioned since the percentage of recovered chloronitrobenzene is greatest with ortho and para chloronitrobenzene; this indicated that some factor inhibits the reduction of the nitro group.

The temperature conditions for the reduction by dextrose were those found by Opolonick (13) to give the best yields of azoxybenzene, viz., a fairly low temperature during the addition of the dextrose, followed by a higher temperature for the remainder of the reaction. The yield of the crude azoxy compound is given in those cases where the product is slightly dark but easily purified. It may be noted that the use of dextrose in alkaline solution can be expected to be a good method for the preparation of the amine when the solution is more dilute. Such an example is found in Expt. 9, Table I.

The reaction for the reduction of a nitrobenzene compound by sodium arsenite is:



In practice an excess of sodium arsenite, as well as a still greater excess of sodium hydroxide, is used to increase the yield. In some experiments methyl alcohol was added to the chloronitrobenzene - sodium arsenite mixture in an attempt to improve conditions by increasing the solubility of the chloronitrobenzene compound. In two experiments, by the reduction of 2-chloronitrobenzene and 2,5-dichloronitrobenzene, an entirely new product appeared, which is a hydroxyazo compound. The analysis of the product produced by the reduction of 2-chloronitrobenzene indicates that it is an isomer of 2,2'-dichloroazoxybenzene. It was not studied further except to note that its physical constants do not correspond to those of 4-hydroxy-2,2'-dichloroazobenzene.

To gain experience we carried out reduction of chloronitrobenzene compounds by these reducing agents: magnesium in methyl alcohol (15), magnesium in methyl alcohol and saturated ammonium chloride solution (14), zinc dust in alcohol and saturated ammonium chloride solution (5), sodium methoxide in absolute alcohol, sodium ethoxide in absolute alcohol, and potassium hydroxide in absolute alcohol. We found that reduction by dextrose or by sodium arsenite had the advantages of producing better yields and a product more easily purified.

Experimental

Reduction of a Chloronitrobenzene Compound. Tables I, II, and III

In each case the experimental conditions are found in the tables. At the end of the reaction time any alcohol present was removed by distillation. The remaining solution was then steam distilled from basic solution until no further solids appeared in the steam distillate. This required 3 to 24 hr., the actual time depending on the amount of the amine and unchanged chloronitrobenzene present in the mixture and on the vapor pressure of these products.

The residue remaining from the steam distillation in the dextrose reduction was digested with large volumes of hot water to remove water soluble impurities. When the azoxy compound was very black or dark red, as in Expts. 3, 4, and 9, Table II, it was first washed with cold alcohol, in which the azoxy compound is only very slightly soluble. This treatment removes most of the tars. In other cases, as in Expt. 7, Table II, the azoxy compound was dissolved in benzene and warmed for a short time with charcoal to remove tars. Any remaining red substance, as in Expts. 3, 4, and 9, Table II, was removed by digesting in portions with a large volume (2 to 10 liters) of a dilute solution of sodium hydroxide or sodium carbonate. The filtrate containing the hydroxyazo compound was made acid. The red precipitate formed was removed by filtration, and, when dry, it was crystallized from

TABLE I
REDUCTION OF SOME NITROBENZENE COMPOUNDS* BY DEXTROSE

Expt. No.	Substituent	% recovery	Reagents			Reaction conditions: time, hr. temp., °C.	Azoxy, % yield	Other products, % yield
			Dextrose, moles	NaOH, moles	H ₂ O, ml.			
1	2-Chloro	42	0.25	1.5	200	1/70 + 2/90	27c, 8r	—
2	3-Chloro	0	0.23	1.5	200	1/60 + 2/110	51 c	—
3	4-Chloro	45	0.23	1.5	200	3/109	22.6 c, 12 r	—
4	2,5-Dichloro	0	0.23	1.5	300	3/90	25 c	—
5	3,4-Dichloro	20	0.23	1.5	300	1/70 + 2/85	20 c	—
6	Same	17	0.5	1.5	800	1/60 + 2/110	17 c	Amine (0.5 gm.)
7	2-Methyl-3-chloro	98	0.23	1.5	200	1/70 + 2/109	2 c	—
8	Same	26	0.6	1.5	300	1/70 + 2/109	25.4 c	Amine, 4.5
9	2-Methoxy-5-chloro	1.5	0.6	1.5	300	1/70 + 2/109	49 c	Amine, 21

* The amount of nitrobenzene compound used in each case was 0.33 mole.

Note: (a) Mechanical stirring in each case.

(b) Dextrose added during first hour, in small portions.

(c) % yield = % of the theory.

(d) c = Crude.

r = Refined.

TABLE II

REDUCTION OF SOME NITROBENZENE COMPOUNDS* BY SODIUM ARSENITE

Expt. No.	Substituent	% re-covery	Reagents				Reaction conditions: time, hr. / temp., °C.	Azoxy, % yield	Other products, % yield
			As ₂ O ₃ , moles	NaOH, moles	H ₂ O, ml.	CH ₃ OH, ml.			
1	2-Chloro	45	0.275	1.5	200	—	8/75	7 r	—
2	Same	57	0.275	1.7	200	—	8/90	11 c	—
3	Same	9	0.275	1.7	300	200	8/90	10 c	Hydroxyazo, 5
4	Same	14	0.250	1.5	125	250	6/48	7 c	Amine, 21, Hydroxyazo, 9
5	3-Chloro	9	0.275	1.7	180	—	8/90	82 c	—
6	4-Chloro	9	0.275	1.7	200	—	8/109	48 c	—
7	2,5-Dichloro	0	0.275	1.7	300	—	8/105	9 c	Amine, 14
8	Same	18	0.275	1.6	200	—	8/90	21 c	—
9	Same	11	0.284	1.62	60	60	6/74	26 c	Hydroxyazo (1.9 gm.)
10	3,4-Dichloro	25	0.275	1.7	200	—	10/85	35 c, 24 r	—
11	2-Methyl-3-chloro	0	0.275	1.7	200	—	8/109	0	Amine, 12
12	Same	61	0.275	1.7	200	100	5/79	14 r	Amine, 5
13	Same	56	0.275	1.7	300	100	8/79	6 c	—
14	2-Methoxy-5-chloro	13	0.275	1.7	200	200	8/79	36 r	Amine, 10

* The amount of the nitrobenzene compound used in each case was 0.33 mole.

Note: (a) Mechanical stirring in each case.

(b) % yield = % of theory.

(c) Stoichiometric proportions: Nitrobenzene compound, 0.33 mole; arsenic trioxide, 0.25 mole; sodium hydroxide, 1.5 moles.

(d) c = Crude.

r = Refined.

benzene. The azoxy compound after treatment with the cold alcohol and the dilute basic solution was fairly pure and was recrystallized several times from a mixture of alcohol and benzene.

The steam distillate consists of unchanged chloronitrobenzene and any amines formed. The solids in the steam distillate were digested in acid solution and filtered. The residue was unchanged chloronitrobenzene. In some cases the residue from the acid digestion was an oily liquid from which the chloronitrobenzene crystallized only after standing in the ice box for several days. The amine was precipitated by making the acid solution basic. When the amine was a liquid or was present in small amounts, as in Expt. 6, Table I, the basic solution was extracted with ether. The ether extracts were evaporated and the residue converted into the acetyl derivative for the determination of the melting point or for analysis in doubtful cases.

The solution remaining from the steam distillation was made neutral and extracted with ether. In no case was more than a trace of a phenol found.

TABLE III

AZOXYBENZENES PRODUCED BY REDUCTION OF SUBSTITUTED NITROBENZENES

Compound	Formula	M.p., ° C. (un-corrected)	Color	Analysis	
				Calc.	Found
2,2'-Dichloroazoxybenzene	$C_{12}H_9ON_2Cl_2$	56 ^a	Pale yellow	N, 10.48 C, 53.95 H, 3.01 Cl, 26.54	10.43 53.93 3.08 26.57
3,3'-Dichloroazoxybenzene	$C_{12}H_9ON_2Cl_2$	97 ^b	Dark yellow	Cl, 26.54	25.78
4,4'-Dichloroazoxybenzene	$C_{12}H_9ON_2Cl_2$	155 ^c	Light yellow	Cl, 26.54	25.53
2,2',5,5'-Tetrachloroazoxybenzene	$C_{12}H_6ON_2Cl_4$	147 ^d	Faint yellow	N, 8.63	7.35
3,3',4,4'-Tetrachloroazoxybenzene	$C_{12}H_6ON_2Cl_4$	139 ^e	Lemon yellow	Cl, 42.20	41.38
2,2'-Dimethyl-3,3'-dichloroazoxybenzene	$C_{14}H_{11}ON_2Cl_2$	122-123 ^f	Faint yellow	Cl, 24.02	23.41
2,2'-Dimethoxy-5,5'-dichloroazoxybenzene	$C_{14}H_{11}O_2N_2Cl_2$	119 ^g	Brownish yellow	Cl, 21.67	22.99

^a Ref. (4) 56° C.^b Ref. (10) 97° C.^c Ref. (8) 155° to 156° C.^d Ref. (7) 147° C.^e Ref. (6) 137° to 138° C.^f New compound.^g New compound.

A detailed description of one case each of reduction by dextrose and by sodium arsenite follows.

Reduction of 3,4-Dichloronitrobenzene by Dextrose

A mixture of sodium hydroxide (60 gm., 1.5 moles), water (750 ml.), and 3,4-dichloronitrobenzene (63 gm., 0.33 mole) was heated with efficient stirring in a 1-liter, 3-necked flask at 60° to 70° C. for one hour. During this time a syrup of dextrose (45 gm., 0.23 mole) in water (50 ml.) was added in small portions. If necessary the flask was cooled to keep the temperature below 70° C. At the end of the first hour the temperature was allowed to rise to 110° C., at which point it was maintained for the last two hours.

The reaction mixture was then steam distilled until the amount of solid coming over in the steam distillate was negligible. The distillate was made acid, warmed, and filtered. The residue was unchanged 3,4-dichloronitrobenzene. Yield, 11 gm. (17% of the original); m.p., 41° C.

The filtrate was made basic with sodium hydroxide. A light precipitate of 3,4-dichloroaniline was obtained. The mixture was filtered. The clear solution, which smelled of 3,4-dichloroaniline, was extracted with ether. When the ether had evaporated, the residue was added to the 3,4-dichloroaniline precipitated from the solution. Combined yield was 0.5 gm.; m.p.

71° C. Found (Kjeldahl): N, 8.55%. Calc. for $C_6H_5NCl_2$: N, 8.64%. Found (Na_2O_2 fusion): Cl, 43.41%. Calc. for $C_6H_5NCl_2$: Cl, 43.77%.

Acetyl derivative: m.p., 122.5° C. Found (Kjeldahl): 6.56%. Calc. for $C_8H_7ONCl_2$: N, 6.56%. Found (lime fusion): Cl, 34.14%. Calc. for $C_8H_7ONCl_2$: Cl, 34.76%.

The original solution remaining from the steam distillation contained a fairly heavy deposit of brown granular 3,3',4,4'-tetrachloroazoxybenzene, which was removed from the solution by filtration. The azoxy compound was treated with hot water until all water soluble substances were removed. The compound was dried and weighed; yield, 19 gm. (17% of the theoretical). An almost quantitative yield was obtained when the compound was crystallized from a mixture of alcohol and benzene; m.p., 139° C. (For analysis see Table III.)

Reduction of 2-Methyl-3-chloronitrobenzene by Sodium Arsenite

To a thick paste of arsenic trioxide (54.4 gm., 0.275 mole) and water was slowly added with stirring a solution of sodium hydroxide (70 gm., 1.7 moles) and water (200 ml.). The mixture was poured into a 1 liter, three-necked flask. To this mixture was added a warm solution of 2-methyl-3-chloronitrobenzene (57.2 gm., 0.33 mole) dissolved in methyl alcohol (100 ml.). The whole mixture was stirred for five hours at 79° C. A heavy yellow oil slowly formed. At the end of the time the reaction mixture was treated as for reduction by dextrose.

After the steam distillation, a yellow granular deposit of almost pure 2,2'-dimethyl-3,3'-dichloroazoxybenzene was obtained. Yield, 13.5 gm. (14% of the theoretical). The analysis is found in Table III. The acetyl derivative of 2-methyl-3-chloroaniline melted at 157° C. (12). Yield, 3 gm. Found (lime fusion): Cl, 18.55%. Calc. for $C_9H_{10}NOCl$: Cl, 19.31%. Recovered: 34.5 gm. (61% of the original) unchanged 2-methyl-3-chloronitrobenzene; m.p. 37° C.

Acknowledgment

Generous samples of 2-chloronitrobenzene and 2,5-dichloronitrobenzene were received from Monsanto, Ltd. This gift is gratefully acknowledged. One of us (K.F.K.) wishes to express his indebtedness to the late Dr. H. E. Bigelow, then Carnegie Professor of Chemistry, Mt. Allison University, for his valued advice regarding the reduction of 2-chloronitrobenzene and 2,5-dichloronitrobenzene by sodium arsenite. We are indebted to an unpublished thesis by H. J. Hockin, Mt. Allison University, for certain suggestions regarding the reduction of 2-chloronitrobenzene by sodium arsenite.

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THE IDENTIFICATION OF AZOXY COMPOUNDS¹

BY ROGER GAUDRY AND KARL F. KEIRSTEAD

Abstract

An azoxy compound can be treated with concentrated sulphuric acid to produce a hydroxyazo product consisting chiefly of the para isomer. This reaction, the Wallach rearrangement, is the basis for a suggested generic test for an azoxy compound. For the identification of a given azoxy compound, two derivatives are suggested: the hydrazo compound produced by the reduction of the azoxy compound by zinc dust, and the azo compound produced by the oxidation of the hydrazo compound. These compounds are described for the first time: 2,2'-dichloro-4-hydroxyazobenzene, 2,5',2,5'-tetrachloro-4-hydroxyazobenzene, 2,2'-dimethoxy-5,5'-dichloroazobenzene, 3,3',4,4'-tetrachlorohydrazobenzene, 2,2'-dimethyl-3,3'-dichlorohydrazobenzene, and 2,2'-dimethoxy-5,5'-dichlorohydrazobenzene.

Introduction

Most types of compounds have some well developed and convenient method for their identification. In the case of azoxy compounds, the general suggestions found in the literature are too vague for convenient use. As a typical example we find in Shriner and Fuson's text (16, p. 172) the following suggested procedures:

- (1) Reduction of the azoxy compound by tin to a known amine,
- (2) Reduction of the azoxy compound to a known azo compound by suitable reagents.

The first procedure is, of course, not a specific test for an azoxy compound since nitro, azo, and azoxy compounds can all be reduced to an amine by tin. The latter procedure is not given in detail and the table of azo compounds given in Shriner and Fuson's text is not extensive enough to be of much use. It would be desirable then to have (a) a generic test for azoxy compounds, and (b) a table of melting points of derivatives that can be prepared conveniently from azoxy compounds.

The reaction, known as the Wallach rearrangement (18) appears to be well suited as a generic test for azoxy compounds. The reaction consists of the conversion of an azoxy compound into a hydroxyazo compound by the action of concentrated sulphuric acid.

Bamberger (1) showed that a small amount of ortho hydroxyazobenzene was formed as well as the para hydroxyazo compound. Lachman (10), who made the most careful study of the rearrangement of azoxybenzene, reported that 1.5 gm. of 2-hydroxyazobenzene was obtained from the rearrangement of 75 gm. of azoxybenzene. If the para position is occupied, as in 4,4'-dichloroazoxybenzene, the oxygen is removed entirely. In the latter reaction, the product is 4,4'-dichloroazobenzene (7).

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Contribution from the Department of Biochemistry, Faculty of Medicine, Laval University, Quebec, Que.

This rearrangement has been used by some investigators (12, 13, 15, 18) for the preparation of hydroxyazo compounds.

We have studied the Wallach rearrangement and the chief product of a number of chloroazoxybenzene compounds whose preparations are described in a previous paper (6). The condition for each rearrangement and the chief product are shown in Table I.

In each experiment the hydroxyazo compound was carefully purified. Judging from the rearrangement of azoxybenzene (10) and of 4-nitroazoxybenzene (12), we would expect the chief product to be the para hydroxy compound. We attempted to establish the constitution and to judge the purity of the product formed by the rearrangement of 2,2'-dichloroazoxybenzene by preparing, according to the method of Schoutissen (14), 2,2'-dichloro-4-hydroxyazobenzene by coupling diazotized 2-chloroaniline and 3-chlorophenol. A comparison of the physical properties of the compound produced by rearrangement and the compound prepared by synthesis shows fairly good agreement. It is quite certain that the former compound is fairly pure 2,2'-dichloro-4-hydroxyazobenzene.

From all available data, the following procedure is a generic test for azoxy compounds: the compound when treated with a large volume of concentrated sulphuric acid (*a*) becomes bright red and is soluble in the acid, (*b*) is precipitated when the mixture is poured into water, and (*c*) is, after that, fairly soluble in dilute basic solution.

An azoxy compound may be reduced conveniently and quantitatively to a hydrazo compound which, in turn, may easily be oxidized to the azo compound. We suggest that the hydrazo and azo compounds so formed be used as derivatives for the identification of an azoxy compound. A list of azo and hydrazo derivatives of the azoxy compounds described in a previous paper (6) is found in Table II.

Experimental

Wallach Rearrangement

The azoxy compound (10 gm.) was rapidly mixed with concentrated sulphuric acid (100 gm.). The mixture rapidly became red. However, this color does not necessarily indicate that the reaction has gone very far. Where necessary the mixture was warmed on a water bath. After heating for the minimum time as indicated by several trials, the mixture was poured into an excess of water. The precipitated solid was digested with a large volume of dilute sodium carbonate solution (2 to 10 liters). The dark residue of polymerized products remaining after this treatment was discarded. The free hydroxyazo compound was precipitated by making the combined filtrates neutral by addition of hydrochloric acid. The precipitated hydroxyazo compound was colloidal; this made ordinary suction filtration almost impossible. After the mixture was allowed to stand for some time most of the liquid was decanted. The remainder of the liquid was removed by allowing the mixture to stand overnight in a large Büchner funnel. After the residue had dried, the compound was purified by repeated precipitation from a mixture of alcohol

TABLE I
CHIEF COMPOUND PRODUCED BY WALLACH REARRANGEMENT

Substituents	Conditions	M.p., °C., uncor- rected	Color	Formula	Analysis		Derivative
					Calc.	Found	
2,2'-Dichloro- (4-hydroxy)	Cold conc. H ₂ SO ₄	^b 174 (185)	Light brown	C ₁₂ H ₈ ON ₂ Cl ₂	Cl, 26.54	25.38	Benzoyl, m.p. 132°C.
2,2'-Dichloro- 4-hydroxy	*	178 (183)	Light brown	C ₁₂ H ₈ ON ₂ Cl ₂	—	—	^a Benzoyl, m.p. 152°C.
3,3'-Dichloro	30 min. in conc. H ₂ SO ₄ , 150°C.	125	Brown	C ₁₂ H ₈ ON ₂ Cl ₂	—	—	—
^c 2,2',5,5'-Tetra- chloro (4-hyd- roxy)	20 min. in conc. H ₂ SO ₄ , 100°C.	191	Red	C ₁₂ H ₆ ON ₂ Cl ₄	Cl, 42.20	41.41	Benzoyl, m.p. 210°C.
3,3',4,4'-Tetra- chloro	20 min. in conc. H ₂ SO ₄ , 100°C.	202	Yellow	C ₁₂ H ₆ ON ₂ Cl ₄	—	—	—
2,2'-Dimethyl- 3,3'-dichloro	20 min. in conc. H ₂ SO ₄ , 100°C.	163 (157)	Brown	C ₁₄ H ₁₂ ON ₂ Cl ₂	Cl, 24.02	25.81	—

* By synthesis.

^a Found: Cl, 19.62%. Calc. for C₁₂H₁₂N₂Cl₂O₂: Cl, 19.10%.

^b Melting point varies with rate of heating.

^c Structure determined by identification of products produced by reduction of the compound by stannous chloride.

and benzene until a constant melting point, under the same conditions, was reached. The melting point depends somewhat on the rate of heating.

Hydrazo Derivative of the Azoxy Compound

The azoxy compound (10 gm.) was dissolved in the minimum amount of alcohol to which 40% solution of sodium hydroxide (35 ml.) was added. The mixture was refluxed on a steam bath with excess zinc dust. The mixture became red in a short time. The heating was continued for several hours until the solution became colorless or almost so. The solution was removed from the zinc by decantation. After the solution had cooled, the hydrazo compound was precipitated by the addition of a small amount of water. If the precipitate had more than a trace of color, it was dissolved in alcohol containing a few drops of acetic acid and warmed with a little zinc dust for a few minutes, after which the colorless hydrazo compound was precipitated as before, and dried in a vacuum desiccator.

Azo Derivative of the Azoxy Compound

The hydrazo compound was dissolved in alcohol and oxidized by boiling in the open air or by bubbling air through the warm solution. The azo compound, being less soluble than the hydrazo compound, readily settles out of the alcohol.

TABLE II

AZO AND HYDRAZO DERIVATIVES OF CERTAIN AZOXY COMPOUNDS

Substituents	Azobenzene		Hydrazobenzene	
	Formula	M.p., °C.	Formula	M.p., °C.
2,2'-Dichloro	C ₁₂ H ₈ N ₂ Cl ₂	136 ^a	C ₁₂ H ₁₀ N ₂ Cl ₂	87 - 88 ^b
3,3'-Dichloro	C ₁₂ H ₈ N ₂ Cl ₂	99 ^b	C ₁₂ H ₁₀ N ₂ Cl ₂	94 ⁱ
4,4'-Dichloro	C ₁₂ H ₈ N ₂ Cl ₂	185 - 186°	C ₁₂ H ₁₀ N ₂ Cl ₂	122 ^j
2,2',5,5'-Tetrachloro	C ₁₂ H ₆ N ₂ Cl ₄	188 - 189 ^d	C ₁₂ H ₈ N ₂ Cl ₄	124 ^k
3,3',4,4'-Tetrachloro	C ₁₂ H ₆ N ₂ Cl ₄	157°	C ₁₂ H ₈ N ₂ Cl ₄	136 - 137 ^l
2,2'-Dimethyl-3,3'-dichloro	C ₁₄ H ₁₂ N ₂ Cl ₂	154 ⁱ	C ₁₄ H ₁₄ N ₂ Cl ₂	138 - 139 ^m
2,2'-Dimethoxy-5,5'-dichloro	C ₁₄ H ₁₂ N ₂ Cl ₂ O ₂	201 ^e	C ₁₄ H ₁₄ N ₂ Cl ₂ O ₂	118 ⁿ

^a Ref. (2), 136° C. Calc.: Cl, 28.10%. Found: Cl, 28.01%.^b Ref. (11), 101° C.^c Ref. (19), 185° to 186° C.^d Ref. (4), 189° C.^e Ref. (9), 195.5° C. (impure).^f Ref. (3), 154° C. Calc.: Cl, 25.40%. Found: Cl, 26.05%.^g New compound. Calc.: Cl, 22.79%. Found: Cl, 21.55%.^h Ref. (17), 87° to 88° C.ⁱ Ref. (11), 94° C.^j Ref. (8), 122° C.^k Ref. (5), 123.5° C. Ref. (4), 117° C.^l New compound. Calc.: Cl, 44.03%. Found: Cl, 43.60%.^m New compound. Calc.: Cl, 25.22%. Found: Cl, 23.98%.ⁿ New compound. Calc.: Cl, 22.69%. Found: Cl, 21.65%.

A second crystallization from alcohol gave a pure azo compound with a sharp melting point.

2,2'-Dichloro-4-hydroxyazobenzene

2-Chloroaniline (3 gm.) was dissolved in concentrated sulphuric acid (15 ml.). To this solution, cooled to 0° C., was added nitrosylsulphuric acid, which was prepared by mixing concentrated sulphuric acid (15 ml.) with sodium nitrite (3.5 gm.) with cooling and mechanical stirring to keep the temperature of the mixture between 0° and 10° C. The temperature was kept below 10° C. while concentrated phosphoric acid (50 ml.) was added with vigorous mechanical stirring. After 30 min., powdered urea (2 gm.) was added to decompose excess nitrous acid, and the solution was poured on cracked ice. The faintly yellow solution was poured slowly, with cooling, into a mixture containing 3-chlorophenol (3 gm.) and sodium hydroxide (214 gm.).

After standing for a few minutes, the soluble portion was removed by boiling with water (3 × 400 ml.). A dark brown residue, with high melting point, remains. Dilute hydrochloric acid was added to the solution containing the water soluble portion. The precipitate was purified in the same way as the similar compounds prepared by the Wallach rearrangement.

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REDUCTION OF STEROIDS USING LITHIUM ALUMINUM HYDRIDE¹

BY G. PAPINEAU-COUTURE, E. M. RICHARDSON², AND GORDON A. GRANT

Abstract

Lithium aluminum hydride has been used successfully in the partial reduction of phthalic anhydride to phthalide, in the selective reduction of the carbonyl group of dehydroisoandrosterone-3-acetate, and in the reduction of oestrone acetate to α -oestradiol without simultaneous production of the β -isomer. A new reduction product of Δ^5 -3(β)hydroxyetiobilienic acid, $\Delta^{5,14}$ -2,13-dimethyl-7(β)hydroxy-2-hydroxymethyl-1-hydroxyethyl dodecahydrophenanthrene, is also described.

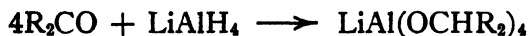
Introduction

It is often desirable to reduce the carbonyl group of esterified ketosteroids without hydrolyzing or reducing the ester group. In general, usual reagents such as zinc-hydrochloric acid or aluminum isopropylate give relatively low yields. These reactions are slow and are carried out in the presence of an excess of the reagent, so that several simultaneous reductions can take place. The properties of the recently discovered lithium aluminum hydride (LiAlH_4) suggested that it might be a more selective reducing agent.

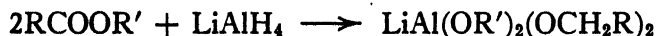
Lithium aluminum hydride was first synthesized by Finholt, Bond, and Schlesinger (2). Its use as a reducing agent in organic chemistry was first reported by Brown, Finholt, Nystrom, and Schlesinger at the New York meeting of the American Chemical Society in September 1946. Further work by Nystrom and Brown (6) has shown that this reagent reduces aldehydes, ketones, esters, acid chlorides, anhydrides, and acids to the corresponding alcohols in ether solution at room temperature.

Typical reductions with reducible groups can be represented by the following equations (6):

Aldehydes or Ketones



Esters



Acid Chlorides



Acid Anhydrides



The lithium aluminum complex forms almost instantaneously and precipitates out of the ether solution. Subsequent treatment with water splits the complex into the alcohol, lithium hydroxide, and aluminum hydroxide.

¹ Manuscript received June 16, 1949.

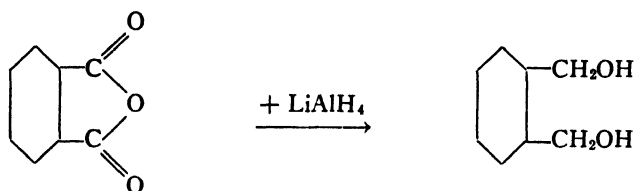
Contribution from the Research Laboratories, Ayerst, McKenna & Harrison, Montreal.

² Present address: Maloney Clinic, Philadelphia 4, Pa.

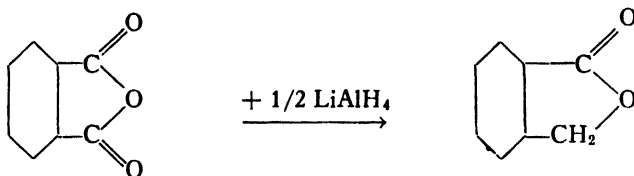
It was thought that because of these properties, lithium aluminum hydride would be a useful reagent in partial reductions such as those mentioned above. In fact, if lithium aluminum hydride is added slowly to an ether solution of the substance to be reduced, the concentration has no chance to build up, since it is used almost immediately upon addition. Moreover, since the complex is insoluble in ether, the most reactive of the reducible groups would be the first and only one to react provided no excess of the reagent is added over the theoretical amount.

The partial reduction of phthalic anhydride to the lactone phthalide was chosen as a model reaction to verify the above hypothesis.

Complete reduction of phthalic anhydride to phthalyl alcohol would require one mole of lithium aluminum hydride.



When one half mole of lithium aluminum hydride is slowly added to one mole of the anhydride, if the above reasoning is correct, the only product will be phthalide:



Whereas if, contrary to the hypothesis, the complex formed by the reaction of one carbonyl group is still reactive, the product should be a mixture of phthalyl alcohol, phthalide, and unreacted phthalic anhydride.

Experimental

Reduction of Phthalic Anhydride to Phthalide

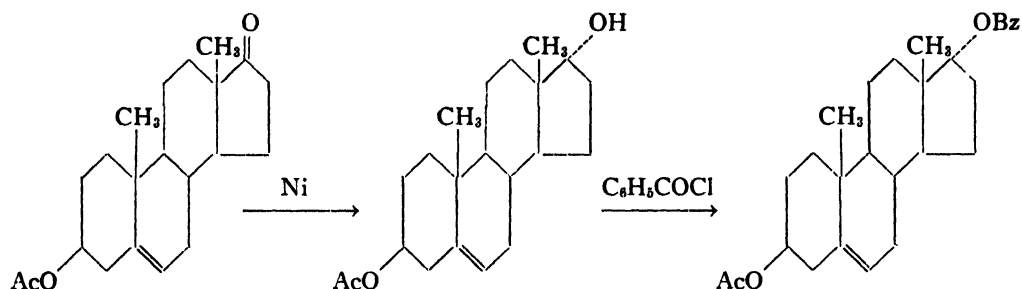
The reduction was done as follows. Phthalic anhydride was dissolved in carefully dried ether and placed in a three-necked flask fitted with a dropping funnel, a stirrer and mercury seal, and a reflux condenser protected by a calcium hydroxide drying tube. An ether solution containing one half mole of lithium aluminum hydride per mole of phthalic anhydride was added dropwise through the funnel, with stirring. When all the reagent had been added, the mixture was cooled in an ice bath, water added, and the mixture was acidified with dilute sulphuric acid to dissolve aluminum hydroxide. The mixture was then transferred to a separatory funnel, the ether phase was separated, and the aqueous phase extracted exhaustively with ether. From the ether, there was obtained a 45% yield of phthalide. No phthalyl alcohol or phthalic anhydride could be identified. It is possible that phthalyl alcohol

remained in the water used to decompose the lithium aluminum hydride complex. However, the result looked promising and no attempt was made to improve the yield.

A similar result was obtained by reacting monomethyl phthalate with three-quarters of a mole of lithium aluminum hydride (one-quarter of a mole being required for the active hydrogen of the free carboxyl group).

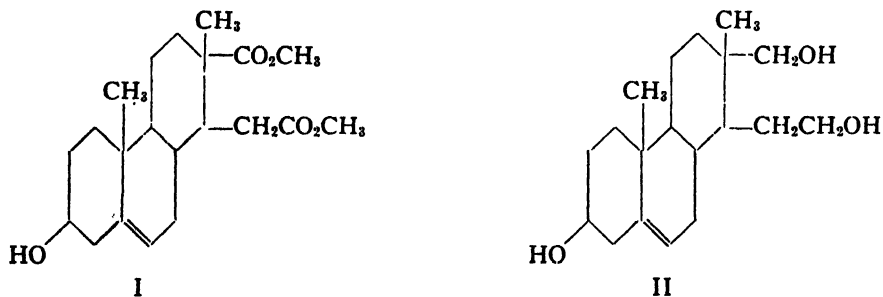
Reduction of Dehydroisoandrosterone Acetate to Δ^5 -androstenediol-3-acetate

This reaction is a step in the synthesis of testosterone from dehydroisoandrosterone. Ruzicka (8) accomplished it by reducing dehydroisoandrosterone acetate with a nickel catalyst, then benzoylating the crude reduction product:



In the authors' hands, with Raney nickel prepared by digestion at 50°C ., the reaction has given yields of about 50%; with lithium aluminum hydride, the reaction was carried out in the manner described above for phthalic anhydride, using a 1 : 4 molar ratio of lithium aluminum hydride to the ester. The crude product obtained by evaporation of the ether extract was benzoylated to pyridine at room temperature and after one recrystallization an 80% yield of Δ^5 -androstenediol-3-acetate-17-benzoate, m.p. 169° to 174°C ., was obtained.

Reduction of Δ^5 -3(β)hydroxyetiobilienic Acid Dimethyl Ester



Δ^5 -3(β)hydroxyetiobilienic acid dimethyl ester (I) has been prepared by Wettstein *et al.* (9) and Kuwada (3). In the course of an investigation of the physiological properties of different derivatives of this acid, it was desired to obtain the completely reduced trihydroxy alcohol $\Delta^9,14$ -2,13-dimethyl-7(β)hydroxy-2-hydroxymethyl-1-hydroxyethyl-dodecahydrophenanthrene (II). Since the ester had to be reduced completely the procedure was modified as follows.

An excess of lithium aluminum hydride in ether solution was placed in the reaction flask and an ether solution of the ester was added at such a rate that the ether kept refluxing. The mixture was refluxed for one-half hour after the addition was complete. After cooling, the complex was decomposed with dilute acid and owing to the low solubility of the product in ether it was extracted with *n*-butanol. The residue obtained by evaporating the solvent *in vacuo* was recrystallized from acetone-hexane; this yielded white crystals melting at 196° to 198° C. (corr.), (α)_D = -63° (alc.). The total yield was 84% of theory. Calc. for C₁₈H₃₂O₃, C = 73.98; H = 10.46%. Found: C = 73.80, 74.04; H = 10.76, 10.80%. The tribenzoate was prepared, using benzoyl chloride in pyridine at room temperature. After two recrystallizations from acetone-methanol, the tribenzoate melted at 133° to 136° C. (corr.). Calc. for C₄₀H₄₄O₆, C = 77.42; H = 7.10%. Found: C = 77.23, 77.43; H = 7.44, 7.42%. (α)_D = -14.5° (chloroform).

Reduction of Oestrone to α -Oestradiol

Oestrone has been reduced to oestradiol by different methods (4, 5, 10) and the product obtained is generally a mixture of two epimers. Since the α -epimer possesses a much greater physiological activity than the β -epimer (10), it is desirable to use a reduction method that yields principally α -oestradiol. With lithium aluminum hydride, oestrone was used as the acetate, which is appreciably more soluble in ether. With an excess of the reagent as described above for etiobilienic acid ester, it gave a 95% yield of α -oestradiol melting at 173° to 176° C., (α)_D +74°.

The absence of β -oestradiol was demonstrated, the method of Carol and Molitor (1) being utilized. These authors have developed a modification of the Kober test to distinguish between α - and β -oestradiol. In the *standard* Kober test, the sample of oestrogen is first heated in boiling water for 20 min. with the reagent, then diluted with an equal amount of water, and heated again for three minutes. These investigators have found that when the 20 min. reaction is done at room temperature (*cold* Kober test), α -oestradiol or oestrone gives very little color upon the final three minute heating, whereas β -oestradiol gives full color development, i.e., same intensity as that given by oestrone or α -oestradiol in the *standard* Kober test. The crude α -oestradiol obtained by lithium aluminum hydride reduction was tested by the *cold* Kober assay and compared with oestrone, β -oestradiol, and a commercial sample of α -oestradiol. The results are given in graphical form in Fig. 1. Obviously, the commercial sample contains appreciable quantities of the β -isomer, whereas the substance obtained by lithium aluminum hydride reduction does not contain more than a trace of β -oestradiol. Since this work has been completed, similar results were reported by Ott and Murray (7, p. 17K) for the reduction of oestrone methyl ether with lithium aluminum hydride.

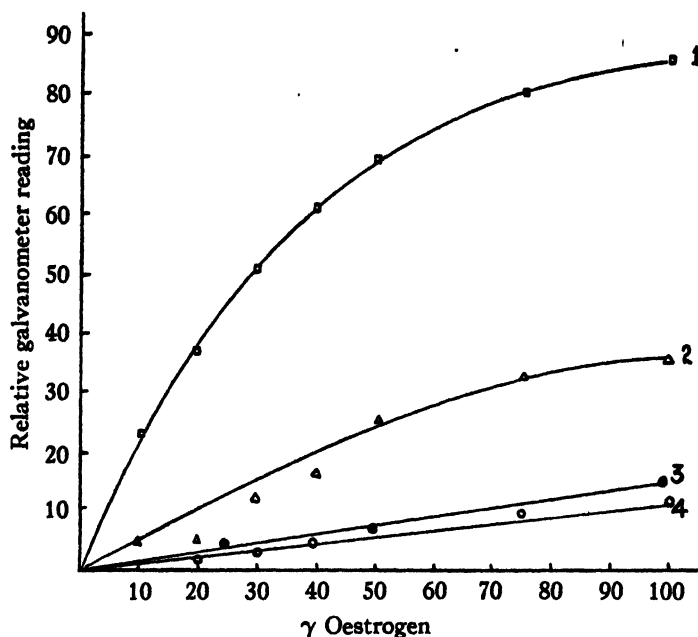


FIG. 1. Cold Kober test on oestrogens.

- 1 (Squares) β -oestradiol
- 2 (Triangles) α -oestradiol (commercial sample)
- 3 (Filled circles) α -oestradiol (LiAlH_4 reduction)
- 4 (Circles) Oestrone.

Acknowledgments

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DETERMINATION OF CELLULOSE IN STRAW HOLOCELLULOSE¹

BY G. A. ADAMS AND A. E. CASTAGNE

Abstract

Hydrolysis of wheat, oat, rye, and flax holocelluloses with 0.5% sulphuric acid for one hour at 100° C. gave a residue that was quantitatively equal to the Cross and Bevan cellulose from the same straws. The hydrolyzed holocellulose residue contained more lignin and less pentosan than the corresponding Cross and Bevan cellulose, but 'pure' cellulose contents (cellulose corrected for ash, lignin, and pentosan) were very similar for both materials; the α -cellulose contents for the two fractions were also equivalent and were slightly higher than the 'pure' cellulose. The α -cellulose contents of the holocellulose were higher than either the Cross and Bevan cellulose or the hydrolyzed holocellulose residue when calculated on the basis of the original straw. The hydrolysis method has the advantage of permitting consecutive determination of holocellulose, cellulose, and α -cellulose on the same sample of straw.

Introduction

Increasing interest in the holocellulose fraction of woods and nonwoody plants has led to the development of several methods for the isolation of this fraction (10, 13, 14, 16). On removing the easily hydrolyzable fraction of spruce holocellulose with dilute acid, Kurth and Ritter (3) obtained a residue that was very similar to Cross and Bevan cellulose. The original procedure was later modified by Van Beckum and Ritter (14) and applied to nine different wood holocelluloses. Increasing the acid strength and hydrolysis time yielded a cellulosic fraction that was quantitatively equivalent to Cross and Bevan cellulose. Further study by Van Beckum and Ritter (15) on aspen, balsam fir, eastern hemlock, jack pine, red spruce, and white spruce showed that holocellulose could be hydrolyzed to a cellulosic fraction comparable in yield to Cross and Bevan cellulose but differing in pentosan content.

While the hydrolysis of holocellulose has been successfully applied to the determination of cellulose in wood, no similar application appears to have been made on cereal straws. Some preliminary experiments in this laboratory showed that the described conditions for hydrolysis when applied to straw holocellulose were too severe. It appeared worthwhile therefore to establish the conditions required for successful applications to straw holocellulose. In addition, a comparison was made between the major constituents of the hydrolyzed holocellulose and of Cross and Bevan cellulose.

Materials and Methods

Clean mature wheat, oat, rye, and flax plants were harvested from experimental plots. The heads were removed but the leafy structures were retained with the straight stem sections. The materials were ground in a Wiley mill

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and then sized in a Rotap screener, using Tyler standard screens. The fraction passing 40 mesh and retained on 60 mesh was used in the subsequent investigations.

Holocellulose was prepared by delignification of the straws with acidified sodium chlorite as previously described (2); Cross and Bevan cellulose content of straw was determined by the Norman and Jenkins hypochlorite method (6). The following methods of analysis were applied to straw, hydrolyzed holocellulose, and Cross and Bevan cellulose: lignin by the 72% sulphuric acid method of Ritter, Seborg, and Mitchell (11); pentosan as furfural determined photocolormetrically (1); α -cellulose as described by Ritter (9); ash by incinerating at 550° C.; and moisture by drying to constant weight at 100° C. *in vacuo*. Samples that had been oven dried were not used for any subsequent analysis except ash.

Experimental Procedures and Results

Holocellulose was isolated from each of the straws in approximately 50 gm. lots. The yields for these quantities compared very closely with the analytical results from 2.0 gm. samples given in Table I. Flax proved most difficult to

TABLE I
COMPOSITION OF STRAWS, % (DRY BASIS)

	Wheat	Oat	Rye	Flax
Ash	4.67	8.85	4.71	2.68
Lignin (apparent)	23.00	22.26	23.05	21.52
Lignin (ash free)	21.33	19.72	22.20	21.52
Pentosan	27.45	22.67	24.15	21.44
Holocellulose	71.0	69.3	66.0	71.0

delignify and required six chlorite treatments to reduce the lignin to 1.10% (ash free). The ash-free lignin contents of the wheat, oat, and rye holocellulose samples were 2.13%, 2.42%, and 2.40% respectively. These values are considerably higher than those previously reported (1); sample trials showed, however, that the use of unextracted straws compared with extracted straws accounted almost entirely for the difference. The lignin, ash, pentosan, and holocellulose contents of various straws reported in Table I show satisfactory agreement with earlier data (8, 12).

Since a comparison was to be made between Cross and Bevan cellulose and hydrolyzed holocellulose it seemed desirable to prepare both materials from the same starting material, i.e., holocellulose. However, the Norman and Jenkins hypochlorite procedure for the preparation of Cross and Bevan cellulose was much too drastic when applied to holocellulose. A series of experiments using milder procedures was therefore conducted (Table II). Extraction of wheat holocellulose with boiling 3% sodium sulphite produced only a minor reduction in weight. Combination of the sulphite extraction with neutral

TABLE II

YIELDS OF CRUDE CELLULOSE OBTAINED BY CHLORINATION AND SULPHITE EXTRACTION OF WHEAT HOLOCELLULOSE

(Based on dry straw having a Cross and Bevan cellulose content of 56.2%)

Treatment	Yield of cellulose, %	Treatment	Yield of cellulose, %
None	72.0	A BBC	49.3
A	67.4	A C	52.6
A B	51.5	A CC	51.8*
A BB	50.3	A CCC	50.7*

A—Boiled for 20 min. in 3% sodium sulphite solution.

B—Neutral hypochlorite followed by boiling in sulphite.

C—Acidified hypochlorite followed by boiling in sulphite.

* Negative test for lignin.

hypochlorite treatments caused substantial losses in weight, and the residue was about 6% less in weight than the Cross and Bevan cellulose content of the original straw. Application of two neutral and one acid hypochlorite treatments proved to be too severe although the residual material still gave a slight color test for lignin. No acid hypochlorite treatment was found that was mild enough to give a residue corresponding quantitatively to Cross and Bevan cellulose. Since a Cross and Bevan cellulose was not produced by the hypochlorite treatment of holocellulose, it was prepared directly from straw by the Norman and Jenkins method (6); the yield was 56.2%. This value was used as a standard of comparison for cellulose yields from the hydrolysis of holocellulose.

Hydrolysis of Wheat Holocellulose

The main factors affecting the mild hydrolysis of holocellulose to a residue equivalent to Cross and Bevan cellulose include: concentration of acid, time of hydrolysis, and temperature. A standard hydrolysis temperature of 100° C. was adopted. Preliminary trials showed that a boiling water bath gave more consistent results than direct heating. Only sulphuric acid was considered since its nonvolatility is advantageous for long refluxing periods. Concentrations of acid of 1.3% were shown to be unsuitable in preliminary experiments and only lower concentrations were investigated further. Hydrolysis times of one and two hours were studied.

For the following experiments, wheat straw holocellulose was prepared by three acid chlorite treatments. Only air dried samples were used for the proposed cellulose determination. The procedure was as follows. Two grams of the holocellulose was accurately weighed and transferred to a 500 ml. Erlenmeyer flask, placed in a boiling water bath, and 200 ml. of boiling sulphuric acid solution of known concentration by weight added. The solution was then heated under reflux for a fixed period of time. Care was taken to prevent dry material from collecting on the sides of the flask and the water

level in the bath was kept above that of the solution in the flask. At the end of the heating period the solution was filtered at once in a sintered glass crucible (Porosity C) and washed with hot water until the washings were neutral to litmus. Water was further removed by a successive wash with 25 ml. of ethanol and 25 ml. of ether; after a short period of air drying the material was dried to constant weight *in vacuo* at 100° C. The yield of hydrolyzed holocellulose was calculated on the basis of air dry straw. In addition to the above experiments using acid, samples of holocellulose were subjected to a similar treatment with distilled water. The results of the various hydrolyses are given in Table III. The two hour treatments with various

TABLE III

HYDROLYSIS OF WHEAT HOLOCELLULOSE WITH DILUTE SULPHURIC ACID

(Holocellulose yield = 71.0% of original straw; Cross and Bevan cellulose content of straw = 56.2%, dry basis)

Strength of acid, % (wt.)	Yield of holocellulose residue, % (based on dry straw)	
	1 hr. heating	2 hr. heating
0	67.2	66.1
0.4	58.5	51.4
0.5	56.3	51.0
0.6	55.6	50.5
0.7	54.5	50.4
0.8	54.0	50.4
0.9	53.5	50.3
1.0		49.6
1.1		49.5
1.2		49.5

strengths of acid were all too drastic, the yield of hydrolyzed holocellulose being less than the Cross and Bevan cellulose. Hydrolysis with 0.5% sulphuric acid for one hour gave a yield of cellulose that was equal in amount to Cross and Bevan cellulose. These conditions were chosen therefore for further investigations of the wheat hydrolyzed fraction. A systematic study of the hydrolysis conditions was limited to wheat holocellulose since trial experiments indicated similar effects on the corresponding fractions from the other straws.

Hydrolysis of wheat holocellulose with acids of the various strengths for a two-hour period yielded a residue that constituted about 50% of the weight of the straw. The uniformity of yield suggests a constant cellulose fraction that merits further investigation. In yield, it approximates more closely to Cross and Bevan cellulose than to α -cellulose. Moreover, Table II shows that a similar residue was obtained by application of the hypochlorite treatments (acid and neutral) to wheat holocellulose.

Hydrolysis of Dried and Undried Holocellulose

In a routine analysis of straw for holo-cellulose and cellulose the most timesaving procedure is as follows: four weighed samples of straw are delignified to holo-cellulose with acid chlorite; two are dried to determine the holo-cellulose yield and two are thoroughly washed with cold 0.5% sulphuric acid and then hydrolyzed to yield the cellulose fraction. However, in most of the present investigation it was more convenient to prepare a quantity of each holo-cellulose in the air dried state and use it for the acid hydrolysis experiments and subsequent analyses. The following data show that the same cellulose and α -cellulose yields can be obtained from both dried and undried samples of holo-cellulose:

	Crude cellulose, % (dry straw basis)	α -cellulose, % (dry straw basis)
Wheat holo-cellulose (dry)	56.2	38.7
Wheat holo-cellulose (undried)	55.9	38.3

Comparison of Yields and Composition of Cross and Bevan Cellulose and Hydrolyzed Holocellulose

Cross and Bevan cellulose and hydrolyzed holo-cellulose were prepared from straw in 10 gm. lots by methods already described. The samples were air dried. The precision of the Cross and Bevan determination was good, the deviation from the mean being about 0.1%; that of the hydrolyzed holo-cellulose was about 0.3%. Much depends on the precision of the preceding holo-cellulose preparation; if overchlorination has taken place the results are less precise. The composition of the two fractions is shown in Table IV. The yields of Cross and Bevan cellulose and hydrolyzed holo-cellulose agree very closely with each other for each straw. Correction of the various fractions for ash content showed that the celluloses prepared from hydrolyzed wheat, oats, and rye holo-cellulose contained considerably more ash than their corresponding Cross and Bevan celluloses. The ash content of flax fractions proved to be an exception, Cross and Bevan cellulose and hydrolyzed holo-cellulose containing 0.86% and 0.44% respectively. The ash content of wheat, oat, and rye holo-celluloses was higher than that of the straw from which holo-celluloses were prepared (2) and apparently the treatment with dilute sulphuric acid did not reduce it.

The apparent lignins in the crude Cross and Bevan celluloses were relatively low, the order of amount being in general agreement with reported values for straws (5, 6). On an ash-free basis the values for wheat and oat lignins were reduced substantially while rye and flax lignins were ash free. The apparent lignins of the hydrolyzed holo-cellulose were quite high for wheat, oats, and rye. However, their ash content is high, so that the ash-free lignin contents become a better basis for comparison. Nevertheless, they are still more than

TABLE IV

COMPOSITION (%) OF CROSS AND BEVAN CELLULOSE AND HYDROLYZED HOLOCELLULOSE FROM VARIOUS STRAWS

	Wheat	Oat	Rye	Flax
<i>Cross and Bevan cellulose</i>				
Crude cellulose	56.2	52.0	55.6	52.8
Cellulose corrected for ash	55.6	51.5	55.1	52.4
Pentosan in crude cellulose	31.9	29.3	29.5	23.9
Lignin (apparent) in crude cellulose	1.30	2.28	1.60	0.87
Lignin (ash-free) in crude cellulose	1.16	1.97	1.60	0.87
'Pure' cellulose in original straw	36.9	35.2	37.8	39.2
α -Cellulose in crude cellulose	69.5	74.9	71.8	72.8
<i>Hydrolyzed holocellulose</i>				
Crude cellulose	56.1	52.7	55.2	52.3
Cellulose corrected for ash	53.9	49.8	54.1	52.0
Pentosan in crude cellulose	25.6	21.5	21.4	18.2
Lignin (apparent) in crude cellulose	4.48	7.47	5.08	1.48
Lignin(ash-free) in crude cellulose	2.84	3.64	3.65	1.48
'Pure' cellulose in original straw	37.3	34.8	39.5	44.4
α -Cellulose in crude cellulose	70.8	74.4	71.4	68.4

twice as great as the lignin in the Cross and Bevan fractions. In the acid hydrolysis step there is no delignification, and the recovered fraction contains all the lignin present in the holocellulose. Since the residual lignin in holocellulose was of the order of 2 to 3% the amount in the hydrolyzed fraction was proportionately higher. Again the flax lignin was an exception. It was ash-free and while greater in amount than in the corresponding Cross and Bevan fractions it was still relatively low. This low value was due to the six chlorite treatments of the flax straw in the holocellulose preparation that have been found necessary to obtain a lignin content comparable with those of the other holocelluloses (1).

For all straws, the pentosan content of the Cross and Bevan cellulose is approximately 25% higher than that of the hydrolyzed holocellulose. The chlorination procedure used in the preparation of Cross and Bevan cellulose removes not only the lignin but most of the polyuronide hemicelluloses, the cellulosan fraction being largely unchanged (15). The hemicellulose fractions are left almost intact in the preparation of straw holocellulose by acid chlorite. The lower pentosan content of hydrolyzed holocellulose compared with Cross and Bevan cellulose suggests that, in the former, cellulosan material has been removed in addition to the easily hydrolyzed polyuronides. In a comparison of the components of Cross and Bevan cellulose and hydrolyzed holocellulose from various woods, Van Beckum and Ritter found more pentosan in the Cross and Bevan cellulose from aspen while the comparable softwood fractions

had a higher pentosan content in the hydrolyzed holocellulose (14). These observations may be accounted for by the close similarity in chemical composition of hardwoods and cereal straws.

The crude celluloses obtained by both the chlorination of the straws and hydrolysis of their holocellulose have similar α -cellulose contents. The somewhat lower content of α -cellulose in hydrolyzed flax holocellulose indicated degradation during the preparation. While the yield of crude flax cellulose was the same for both fractions it is apparent that the hydrolyzed material was readily susceptible to the solvent action of 17.5% sodium hydroxide. The extensive delignification treatments of the original flax straw with sodium chlorite undoubtedly contributed to this susceptibility. The recovery of equal yields of α -cellulose from Cross and Bevan cellulose and hydrolyzed cellulose shows the feasibility of determining α -cellulose directly from hydrolyzed holocellulose. The determination of holocellulose, cellulose, and α -cellulose can therefore be made in succession from the same sample of straw.

The 'pure' cellulose contents of the fractions are values calculated by correcting crude cellulose for ash, pentosan, and lignin and are expressed on the basis of the original straw. The pure cellulose contents in the Cross and Bevan cellulose and in the hydrolyzed holocellulose are similar for wheat, oat, and rye straws. Flax shows a higher yield in the hydrolyzed holocellulose. The α -cellulose contents of both Cross and Bevan and hydrolyzed holocellulose are higher than their pure cellulose contents. This is probably due to the inclusion of pentosan material in the α -cellulose. Lewis (4) reports that fibrous residues contain as much as 8% more of α -cellulose than of pure cellulose although the reverse is true of wood.

TABLE V
 α -CELLULOSE CONTENT OF VARIOUS CELLULOSE FRACTIONS, %
(Calculated on basis of dry straw)

	Wheat	Oat	Rye	Flax
Holocellulose	40.0	40.4	40.1	39.0
Cross and Bevan cellulose	39.1	39.0	39.9	38.4
Hydrolyzed holocellulose	38.7	38.6	40.0	35.2

In Table V, α -cellulose contents of the crude cellulose fractions were calculated on the basis of original straw. The α -cellulose contents of the holocelluloses for all straws were slightly higher than in either of the other fractions. It is apparent that acid hydrolysis of holocellulose caused a loss in α -cellulose. Flax holocellulose was affected more than the others. The close agreement between the yields of α -cellulose from hydrolyzed holocellulose and Cross and Bevan cellulose indicate that preparation of the latter also involves a small loss of α -cellulose. The differences in α -cellulose contents between the various fractions are similar to those found by Van Beckum and Ritter for

aspen wood (14); the same authors found considerably more α -cellulose in softwood holocellulose than in the corresponding Cross and Bevan and hydrolyzed fractions.

The determination of Cross and Bevan cellulose is empirical in nature and depends on the number and severity of treatments required for delignification. Deviation from the prescribed procedures will cause the isolated residues to vary both qualitatively and quantitatively. The method under the best conditions provides a good but by no means absolute separation of the polyuronides and celluloses. Mild acid hydrolyses of holocelluloses removed not only the polyuronides, which are solubilized in the Cross and Bevan cellulose method, but also caused a mild attack on the celluloses as shown by the lower pentosan content of the cellulosic residue.

Other proposed methods of cellulose determination including the ethanolamine (8) and the ethanol - nitric acid procedures (5) produce similar effects. Recovery of equal yields of α -cellulose from the Cross and Bevan cellulose and the hydrolyzed holocellulose indicated that the main cellulosic component was preserved to the same extent by both methods of analysis. The chlorination method yields useful though empirical information, but the production of a similar fraction by hydrolysis of holocellulose provides an easier and more rapid method of obtaining the same data. The hydrolysis method has the added advantage of providing means of determining holocellulose, cellulose, and α -cellulose in succession on the same sample of straw. Furthermore, the method is readily applicable to large scale preparation of the same materials.

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DETERMINATION OF LIGNIN IN CEREAL STRAWS¹

BY G. A. ADAMS AND A. E. CASTAGNE

Abstract

Determination of lignin in wheat, oat, barley, and rye straw with 64%, 68%, 72%, 76%, and 80% (wt.) sulphuric acid showed that a minimum yield of lignin containing a maximum amount of methoxyl was obtained with the 72% sulphuric acid. In this respect, cereal straws differ from deciduous woods for which 72% sulphuric acid lignin determinations are unsuitable. Comparison of lignin determinations made with 72% sulphuric acid and with 42% fuming hydrochloric acid, on the same straws, after pretreatment with 1.0% hydrochloric acid, showed that the former method preserves a larger proportion of the methoxyl groups. Both methods recovered more total lignin methoxyl from untreated than from treated straws, with the sulphuric acid retaining the larger amount. It is concluded that lignin determination with 72% sulphuric acid on straws untreated with dilute acid yields a residue most representative of the 'true' lignin content, based on the criterion of maximum methoxyl recovery.

Introduction

Of the many methods proposed for the determination of lignin in fibrous plant materials, the 72% sulphuric acid and the 42% fuming hydrochloric acid procedures have been most widely used. Many modifications of time and temperature of digestion have been introduced to minimize the effect of these strong acids on the carbohydrate fraction. Until recently little attention was paid to the concentration of the acid because 72% sulphuric acid had become the generally accepted reagent, although Klason, who developed the method, did not claim general suitability of this concentration for all woody materials (8, 9). Pretreatment of the wood or plant material to increase the accuracy of the lignin determination has been extensively investigated. Waksman and Cordon have pointed out that a short period of dilute acid treatment, sufficient to remove easily hydrolyzable carbohydrates prior to the preparation of acid lignin, is required (18). Norman and Jenkins have also studied the problem in detail and recommend a brief dilute acid hydrolysis treatment before determining lignin (12). Phillips and Goss also accept the principle of acid pretreatment (13). On the other hand, Bamford and Campbell found that xylose, fructose, and sucrose when treated with 72% sulphuric acid at 10° C. for five hours yielded negligible quantities of insoluble residues and were therefore unlikely to interfere seriously in lignin determinations (2). Pretreatment of the plant or wood material with either hot water or dilute acid is rejected by Cohen and Harris on the grounds that both have solvent action on the lignin (5). Ploetz states that the pretreatment of woods is no longer recommended, as dilute acids can remove a portion of the lignin (14). In reviewing the evidence Norman points out that the present information

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does not warrant immediate rejection of the acid hydrolysis pretreatment although doubts as to its suitability are raised (11).

It has been usually considered that the proper concentration of sulphuric acid for lignin determination is that which gives a minimum yield of lignin. If the concentration is too low the polysaccharides remain in the lignin residue; if too high, humic substances are formed by the action of the acid on the carbohydrates and are recovered with the lignin. For many woods, 72% sulphuric acid produces a minimum yield of lignin. However, Freudenberg and Ploetz (6) have found this criterion of minimum yield to fail with linden (*Illex tomentosa*) in a study covering 62.5 to 80.5% sulphuric acid. With red beech (*Fagus sylvatica*) and elder (*Sambucus nigra*) the optimum concentration of acid was found to be 66.5%. They proposed therefore that the term "sulphuric acid lignin" be substituted for "Klason lignin" (72% sulphuric acid lignin) and that the product be characterized by maximum methoxyl content. In a similar study Ploetz (14) found that 66.5 to 75% sulphuric acid gave a constant yield of spruce lignin although the methoxyl reached a maximum only at 75% acid. Some deciduous woods yielded minimum lignin containing maximum methoxyl with 66.5% sulphuric acid. Brauns (3) has also pointed out that the discrepancy between calculated and found methoxyl content for maple lignin is due in part to the inaccuracy of the lignin methods.

The unsuitability of the 72% sulphuric acid method for lignin in deciduous wood raises the question whether or not the same method is applicable to fibrous plant materials, which are quite similar in chemical composition to the hardwoods. While the 42% fuming hydrochloric acid method is frequently used for fibrous plants, a great many lignin determinations on these materials are done by the sulphuric acid method because of its simplicity and convenience.

The purpose of the present study was to investigate the effect of a range of sulphuric acid concentrations (64 to 80%) on the yield of lignin from extracted straws. The methoxyl content of the various isolated lignins was determined, as well as the total reducing sugar and pentosans in the hydrolyzates. For comparison, the lignins were determined in the same straws by the 42% fuming hydrochloric acid method. The effect of pretreatment with dilute acid on lignin yield from extracted straws by both methods of determination was included in the study.

Materials and Methods

Clean mature wheat, oat, barley, and rye straws, harvested by hand from experimental plots, were used in the study. The straws were cut in about 1 in. lengths and then milled in a laboratory hammer mill. The ground material was then sized with standard screens on a Ro-tap screener and the -40 to +60 mesh size retained for use in subsequent experiments. All straws were extracted with 1 : 2 alcohol-benzene and hot water according to the standard TAPPI procedure (16). The extracted straw was analyzed for moisture by

drying to constant weight in a vacuum oven at 100° C. Lignin was determined by the sulphuric acid method described by Ritter, Seborg, and Mitchell (15) and by the standard 42% fuming hydrochloric acid method (1). Pentosans were determined as furfural after distillation with 12% hydrochloric acid according to Hughes and Acree (7), total reducing sugars by the procedure of Underkofler *et al.* (17), methoxyl by the Viëbock and Schwappach volumetric procedure as modified by Clark (4, p. 68), and ash by incinerating at 550° C. The sulphuric acid solutions for lignin determinations were prepared on a percentage by weight basis, titrated with standard alkali, and adjusted to $\pm 0.1\%$.

Experimental Procedures and Results

Effect of Sulphuric Acid Concentration on Lignin Determination

Since the concentration of sulphuric acid was the factor being investigated, other factors that influence the determination were standardized as outlined by Ritter *et al.* (15). Slightly larger samples of extracted straw were used. The concentrations of strong sulphuric acid used were 64.0%, 68.0%, 72.0%, 76.0%, and 80.0%. After hydrolysis, the mixture was allowed to cool to room temperature, filtered on a sintered glass crucible (M porosity), washed free of acid with hot water, air-dried overnight, and then brought to constant weight in a vacuum oven at 100° C. Six separate lignin determinations were made on each straw at each concentration of acid. Agreement between individual analyses showed that it was possible to bulk the samples, and the composite sample was used for ash and methoxyl determinations. The solutions from the dilute acid hydrolyses were combined with the washings from the lignin separation, made to volume, and analyzed for total reducing sugars and furfural. Two of the six test solutions were used for these analyses. The results of the various analyses are given in the tables as follows: Table I, wheat; Table II, oat; Table III, barley; and Table IV, rye.

TABLE I

LIGNIN AND SUGAR DETERMINATIONS (%) IN WHEAT STRAW HYDROLYZED WITH SULPHURIC ACID OF VARIOUS STRENGTHS

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Sulphuric acid	Lignin residue			Hydrolyzate	
	Lignin	Ash-free lignin	Methoxyl in ash-free lignin	Total reducing sugars	Pentosans as furfural
64.0	51.08	49.40	5.1	41.16	20.12
68.0	29.50	27.98	11.9	63.70	20.22
72.0	20.75	19.18	15.2	75.09	20.75
76.0	21.10	19.53	15.0	74.06	19.65
80.0	21.52	19.90	14.1	72.31	19.76

The lignin determination in wheat straw showed that 64% sulphuric acid was insufficient to digest the cellulosic material completely. Somewhat stronger acid solutions dissolved the cellulosic material but it was reprecipitated on dilution of the acid to 3%, and subsequent hydrolyses did not render this material completely soluble. As increasing concentrations of acid were used the lignin value passed through a minimum at 72% acid. The methoxyl content reached a maximum at 72% concentration and accordingly satisfied the criterion of Freudenberg and Ploetz (6), who claim that the most representative lignin has a maximum methoxyl content. The lignin and methoxyl values obtained with less than 72% acid represent contamination with cellulosic residues. Above 72% acid concentration, the lignin content again increases owing to combination with humic substances produced by the action of strong acids on the sugar residues. The lower methoxyl figures, particularly in the 80% acid lignin, may be attributed to admixture with humic substances low in methoxyl content. The change in sugar content of the hydrolyzate supported this view. The sugars reach a maximum with 72% acid. Below 72% there is incomplete hydrolysis of the carbohydrates and above 72% sugars are humidified by the acid and condense with the lignin. There is considerable evidence in the literature to show that such reactions occur (10, p. 169). The relatively small change in the furfural values indicated that the pentose sugars were little affected by the acid treatment. The high pentose content with the lowest concentration of acid showed that the hemicellulose fraction was readily hydrolyzed. The sharp reduction in pentose content of the hydrolysate with 75% and 80% acid as reported by Freudenberg and Ploetz (6) for pine, linden, beach, and elder wood was not found for straws, but the two-day treatment with acid used by these investigators may have caused considerably more decomposition of the sugars.

The results for oat straw as given in Table II show, in general, that it behaved similarly to wheat straw. With increasing acid concentrations the lignin yield passed through a minimum with 72% acid. The maximum

TABLE II

LIGNIN AND SUGAR DETERMINATIONS (%) IN OAT STRAWS HYDROLYZED WITH SULPHURIC ACID OF VARIOUS STRENGTHS

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Sulphuric acid	Lignin residue			Hydrolyzate	
	Lignin	Ash-free lignin	Methoxyl in ash-free lignin	Total reducing sugars	Pentosans as furfural
64.0	50.12	49.41	4.8	41.81	20.84
68.0	30.78	30.11	8.9	64.90	20.74
72.0	18.78	18.06	13.7	74.28	21.76
76.0	19.04	18.36	13.8	73.36	20.40
80.0	19.53	18.86	13.1	71.70	20.04

methoxyl content in the lignin occurred with 76% acid but the difference from the 72% acid lignin was negligible. The maximum sugar and pentosan contents occur at the 72% acid level and indicate a minimum combination of sugar residues with lignin.

In Tables III and IV, the results for barley and rye straws show further that 72% sulphuric acid gives a minimum yield of lignin. For barley straw

TABLE III

LIGNIN AND SUGAR DETERMINATIONS (%) IN BARLEY STRAW HYDROLYZED WITH SULPHURIC ACID OF VARIOUS STRENGTHS

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Sulphuric acid	Lignin residue			Hydrolyzate	
	Lignin	Ash-free lignin	Methoxyl in ash-free lignin	Total reducing sugars	Pentosans as furfural
64.0	46.37	45.89	5.2	46.77	20.97
68.0	35.23	34.75	7.6	61.32	20.69
72.0	17.40	16.83	14.8	73.73	20.89
76.0	17.63	17.06	14.3	77.36	21.34
80.0	18.08	17.51	14.1	73.36	18.75

TABLE IV

LIGNIN AND SUGAR DETERMINATIONS (%) IN RYE STRAW HYDROLYZED WITH SULPHURIC ACID OF VARIOUS STRENGTHS

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Sulphuric acid	Lignin residue			Hydrolyzate	
	Lignin	Ash-free lignin	Methoxyl in ash-free lignin	Total reducing sugars	Pentosans as furfural
64.0	48.71	47.95	6.1	48.27	19.96
68.0	35.12	34.40	8.6	57.01	20.08
72.0	19.48	18.79	15.7	71.44	20.07
76.0	19.65	18.98	15.7	73.15	20.36
80.0	20.32	19.56	15.6	72.91	17.60

the maximum methoxyl content of the lignin occurs with 72% acid although the total sugar and furfural figures were slightly higher with 76% acid. While rye straw gave the lowest lignin yield with 72% acid the methoxyl content of the 76% acid lignin was slightly higher. The total sugar and pentosan contents of the hydrolyzate were at a maximum with 76% acid. These data when taken in conjunction with the small differences between the lignin yield with 72% and 76% acid lead to the conclusion that acid concentrations covering this range would be equally satisfactory for determining lignin in rye straw.

It is apparent that the usually employed 72% sulphuric acid gives satisfactory lignin values with cereal straws. In this respect cereal straws resemble the coniferous woods and differ from the deciduous woods.

Comparison of Lignin Determinations by Two Methods on Straws Pretreated with Dilute Acid

Although it has been shown in the foregoing experiments that 72% was the most satisfactory concentration of sulphuric acid for lignin determination in the cereal straws examined, it seemed worthwhile to compare this method with the 42% hydrochloric acid method, which is a standard procedure for plant materials (1). Both acids are known to form huminlike products with carbohydrates although Phillips and Goss (13) claim that the disturbance caused by hydrochloric acid is less—an observation that Norman attributes to the low temperatures that must be used (10, p. 177). Phillips found about 1% less lignin in extracted wheat straw with the hydrochloric acid method although the methoxyl contents of lignins determined by 72% sulphuric acid and 42% hydrochloric acid were almost the same.

Since the official 42% hydrochloric acid method is applied to extracted straws pretreated with 1% hydrochloric acid, the 72% sulphuric acid procedure was used on similarly prepared straw. Extracted wheat, oat, barley, and rye straws were analyzed by both procedures. Methoxyl and ash contents were determined on the isolated lignins. The results are given in Table V.

The 1% hydrochloric acid treatment removed about 35% of the dry substance from all straws. The sulphuric acid lignins were higher than the hydrochloric acid lignins for wheat, oat, barley, and rye straw by 1.28%,

TABLE V

COMPARISON OF LIGNIN DETERMINATIONS (%) IN STRAWS TREATED WITH 1% HYDROCHLORIC ACID, BY THE 72% SULPHURIC ACID METHOD, AND BY THE 42% FUMING HYDROCHLORIC ACID METHOD

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Determinations	Wheat straw		Oat straw		Barley straw		Rye straw	
	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl
Yield of treated straws	66.2	65.9	64.7	65.0	63.4	63.9	65.6	65.5
Lignin	25.69	24.11	23.69	22.00	22.17	20.72	23.09	21.91
Ash-free lignin	23.63	21.79	22.69	20.91	21.18	19.76	22.12	20.83
Methoxyl in ash-free lignin	16.3	16.1	14.9	15.0	15.6	15.4	17.3	17.3
Ash-free lignin in untreated straws	15.63	14.35	14.68	13.59	13.42	12.62	14.52	13.65
Lignin methoxyl in untreated straws	2.55	2.31	2.19	2.04	2.09	1.94	2.51	2.36

1.09%, 0.80%, and 0.87% respectively (ash-free basis). The ash content in the wheat straw lignins was about twice that of the other straws. The methoxyl contents of the lignins isolated by the two methods agreed closely with each other for all straws. The results reported for wheat straw lignin are very similar to those found by Phillips and Goss (13). If one applies the criterion that a minimal lignin value is the most representative of the true lignin content then the hydrochloric acid method would be chosen. However if the criterion of Freudenberg and Ploetz, that the maximum methoxyl is the best indication of 'true' lignin, is accepted, then the sulphuric acid method would be chosen since the calculated lignin methoxyl (last line Table V) shows that the maximum methoxyl was contained in the sulphuric acid lignin. It is reasonable therefore to conclude that the 72% sulphuric acid method is preferable to the hydrochloric acid method, which gives a lower total lignin methoxyl content.

Comparison of Lignin Determinations on Untreated Straw

Since the usefulness of dilute acid treatment of cellulosic plant materials prior to lignin determination had not been clearly demonstrated, it seemed advisable to compare the two methods of lignin determination on straws that had not been treated with acid. The 72% sulphuric acid and 42% hydrochloric acid methods were therefore applied to wheat, oat, barley, and rye straws after alcohol-benzene and hot water extraction. The results are shown in Table VI.

TABLE VI

COMPARISON OF LIGNIN DETERMINATIONS (%) IN STRAW BY THE 72% SULPHURIC ACID METHOD AND THE FUMING HYDROCHLORIC ACID METHOD

(Straw extracted with alcohol-benzene and hot water, dry wt. basis)

Determinations	Wheat straw		Oat straw		Barley straw		Rye straw	
	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl
Lignin	20.75	18.51	18.78	16.39	17.40	15.20	19.48	16.30
Ash-free lignin	19.18	17.03	18.04	15.60	16.80	14.62	18.82	15.62
Methoxyl in ash-free lignin	15.2	15.3	13.7	14.1	14.8	15.0	15.6	16.7
Lignin methoxyl in straw	2.91	2.60	2.47	2.20	2.49	2.19	2.94	2.61

The sulphuric acid lignins (ash-free basis) were 2 to 3% higher than the hydrochloric acid lignins. The methoxyl contents in the lignins isolated by both methods were very similar, with the exception of rye straw. Although hydrochloric acid yielded a minimum amount of lignin with a slightly higher methoxyl content than the sulphuric acid lignin, calculation of the total methoxyl isolated in the lignin residues from wheat shows that 2.91 - 2.60 =

0.31% more methoxyl was contained in the sulphuric acid lignin. If it is assumed that the higher yield of sulphuric acid lignin ($19.18 - 17.03 = 2.15\%$) was due to the presence of humified carbohydrate, then this excess material would have to contain $\frac{0.31}{2.15} \times 100 = 14.4\%$ methoxyl—an invalid assumption, since it is known that the carbohydrate fraction contains only a small amount of methoxyl. The calculated methoxy content indicates that this material is closely related to lignin. Similar calculations applied to oat, barley, and rye lignins show that the sulphuric acid lignin cannot contain appreciable quantities of carbohydrate residues. On the basis of these results on untreated straws, it is reasonable to conclude that 72% sulphuric acid gives a more truly representative lignin than fuming hydrochloric acid.

Comparison of the data in Tables V and VI shows that the lignins determined by both methods are lower in all straws pretreated with dilute acid, and that pretreatment with acid affected the sulphuric acid method more than the hydrochloric acid method. The methoxyl of the lignins from acid treated straw was higher than from untreated straw. The lower lignin yield from acid treated straws is attributed by Phillips (13) to the removal of interfering substances by the dilute acid. However, if the same calculation as in the preceding section is applied, it is evident that this is not so. Untreated wheat straw contained $19.18 - 15.63 = 3.55\%$ more 'lignin' than the treated straw. However, since the total lignin methoxyl was $2.91 - 2.55 = 0.36\%$ higher in the lignin from untreated straw, then this excess 'lignin' must have a calculated methoxyl content of $\frac{0.36}{3.55} \times 100 = 10.15\%$. Again the value is too high to be attributed to humified carbohydrate material. The same calculation applied to hydrochloric acid lignin from treated and untreated wheat straw shows that untreated straw yields a lignin residue containing more total methoxyl. The increase over that of treated straws cannot be due to humified carbohydrate material. Similar data leading to the same conclusion can be calculated for the other straws. These results lend indirect support to the evidence of Cohen and Harris (5) that a dilute acid pretreatment removes a portion of the lignin.

The proposal of Freudenberg and Ploetz (6) that the criterion for lignin determinations should be a residue with a maximum methoxyl content appears to be justified. It has been shown that the determination of lignin in untreated straws with 72% sulphuric acid more nearly satisfies the requirements of 'true' total lignin than determination with 42% hydrochloric acid. It is also worth noting that the sulphuric acid method is faster and more convenient and avoids the unpleasantness associated with the use of fuming hydrochloric acid.

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DISTRIBUTION OF METHOXYL AND URONIC ACID GROUPS IN CEREAL STRAWS¹

BY G. A. ADAMS AND A. E. CASTAGNE

Abstract

The distribution of methoxyl and uronic acid groups in wheat and oat straw has been investigated in the following successive fractions: extractive-free straw, pectin-free straw, holocellulose, hemicellulose "A", hemicellulose "B", and "α-cellulose" residue. About 18% of the total methoxyl content of extractive-free straws was found in the holocellulose fraction, the remainder being associated with the lignin portion. Methoxyl groups in the hemicellulose fractions and residues accounted for only about 70% of those present in the holocelluloses. No glycosidic methoxyls were found and the amount of ester methoxyl was too small to account for losses by saponification. The conclusion was reached that some of the ether methoxyls were cleaved during the alkali extraction of the holocelluloses. Methoxyl values in the α-cellulose residues as obtained by the Zeisel method were considerably greater than those of the trimethylamine procedure. Uronic acid groups of the extractive-free straw were almost quantitatively accounted for in the various fractions. The molar ratio $\frac{\text{uronic acid anhydride}}{\text{methoxyl}}$, which was less than unity in the holocelluloses, increased to greater than unity in the hemicelluloses A and B of both straws.

Introduction

The presence of methoxyl groups in the cellulosic portion of wood and straws has been clearly established. Ritter and Barbour found approximately 88% and 77% of the methoxyl of red wood and white oak respectively associated with lignin, the remainder being distributed between extraneous material and holocellulose (18). A wheat straw holocellulose isolated by Schenck and Kurth contained 19% of the total methoxyl of the extractive-free straw (21). Kurth and Ritter prepared holocellulose fractions containing 12% of the total methoxyl from extractive-free spruce wood (12). The distribution of the methoxyl groups in various hemicellulosic fractions prepared by alkaline treatment of woods and fibrous plants has received considerable attention. Most of the methods of hemicellulose isolation are empirical and represent a great diversity of alkaline extractions. Many have followed the well known procedure of Norris and Preece (16). While the presence of lignin in the fractions has complicated the interpretation of the methoxyl values, there seems to be general agreement that the methoxyl groups are attached to uronic acids in methoxyhexuronic acid units. In mesquite wood hemicelluloses Sands and Nutter found approximately one methoxyl group per uronic acid molecule (20). On further purification by chlorination, definitely less than one methoxyl per uronic acid was obtained. A molar ratio of uronic acid to methoxyl of 1.6 was found by Sitch (22) for an ethylenediamine soluble fraction of white birch.

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The present investigation was concerned with the distribution of methoxyl groups and uronic acids in various fractions of extractive-free wheat and oat straws. Holocellulose preparations were used to avoid the interference of lignin in the alkali soluble fractions and residues. No attempt was made to separate a variety of hemicellulose fractions but a procedure was used that yields broad hemicellulosic fractions quantitatively. It was hoped, in this way, to follow the preservation and distribution of the methoxyl and uronic acids in empirical but quantitative fractions.

Materials and Methods

Clean mature wheat and oat straw was cut into 1 in. lengths and then ground in a Raymond laboratory pulverizer. The fraction that passed through a 40 mesh screen and was retained on 60 mesh was used in the subsequent investigations. The material was extracted with 1 : 2 alcohol-benzene and hot water according to the standard Tappi method (23). This extractive-free straw was considered as the starting material for this study. Pectin substances were extracted with 0.5% ammonium oxalate by three separate four-hour treatments at 85° C. and the residue was thoroughly washed with water at 40° C. The ammonium oxalate extract was concentrated to one-quarter volume and poured into acidified ethanol to precipitate the pectin. Holocellulose was prepared by the acid chlorite procedure previously described (1). Hemicelluloses were isolated from the holocellulose according to Wise *et al.* (27). Lignin determinations were made by the 72% sulphuric acid method (19). Total methoxyl was determined by Clark's modification of the Viebock and Schwappach procedure (6, p. 68); ester methoxyl by von Fellenberg's method (9, p. 68) and glycosidic methoxyl according to Hoffpauir and Reeves (11) except that the formaldehyde was determined with chromotropic acid instead of Schiff's reagent. Uronic acid was determined by a modification of the method of Dickson *et al.* (8) in which the carbon dioxide produced by decarboxylation was removed by a stream of carbon-dioxide-free nitrogen in an all-glass apparatus. Moisture was determined by drying to constant weight at 100° C. in a vacuum oven; ash by incinerating at 550° C.

Experimental Procedures and Results

Composition of Extractive-free and Pectin-free Straws

The lignin and methoxyl contents of extractive-free wheat and oat straw before and after extraction of pectin by 0.5% ammonium oxalate are given in Table I. As was to be expected, little or no change in either the lignin or methoxyl content of the lignin was found. There was a small decrease in the total methoxyl content of the straw owing to removal of pectin amounting to 0.10% and 0.15% for wheat and oat straw respectively. The calculated methoxyl contents of the isolated pectin fractions were 9.52% for wheat straw and 7.14% for oat straw. However, methoxyl determinations on these materials yielded only about 50% of these values, indicating incomplete recovery of the pectin fraction. The small decrease in uronic anhydride in

TABLE I

COMPOSITION OF EXTRACTIVE-FREE STRAWS BEFORE AND AFTER EXTRACTION OF PECTIN

	Wheat straw		Oat straw	
	Before	After	Before	After
Lignin (ash free), %	19.50	19.54	20.05	20.19
Methoxyl in lignin, %	15.70	15.64	15.40	15.50
Total methoxyl, %	3.72	3.62	3.78	3.73
Lignin methoxyl, %	3.06	3.06	3.09	3.13
Lignin methoxyl, % of total methoxyl	82.4	84.6	81.7	83.8
Methoxyl in cellulosic fraction (by difference), %	17.6		18.3	
Uronic acid anhydride, %, (carbon dioxide \times 4)	2.99	2.94	3.36	3.32
Pectin, %	1.05		0.70	

the pectin-free straws was due to removal of pectin substances. The data for lignin methoxyl permitted calculation, by difference, of the portion of the total methoxyl of the straw that was present in the cellulosic fraction. Values of 17.6% and 18.3% for wheat and oat straw respectively were in reasonable agreement with a value of 19% reported by Schenck and Kurth for wheat straw holocellulose (21). These values are considerably higher than those reported for woods (10, p. 665).

Composition of the Holocelluloses

The yield and partial composition of the holocelluloses prepared from extracted straw are given in Table II. Summation of holocellulose + lignin

TABLE II

METHOXYL AND URONIC ACID CONTENT OF HOLOCELLULOSES PREPARED FROM PECTIN-FREE STRAWS (DRY BASIS)

Yield of holocellulose, %	Wheat straw	Oat straw
	79.8	76.6
Lignin (ash free), %	1.72	2.10
Methoxyl in lignin, %	10.56	9.56
Lignin methoxyl, % (holocelluloses basis)	0.18	0.20
Total methoxyl, %	0.91	1.14
Holocellulose methoxyl, %	0.73	0.94
Holocellulose methoxyl, % (straw basis)	0.58	0.72
Calculated* holocellulose methoxyl (straw basis), %	0.56	0.60
Uronic acid anhydride, %	3.80	4.32
Uronic acid anhydride, % (straw basis)	3.03	3.31

*Total methoxyl of straw minus lignin methoxyl of straw.

accounted for 99.3% of wheat straw and 96.7% of oat straw. Both wheat and oat holocelluloses contained a small amount of lignin. Methoxyl contents of isolated holocellulose lignins were considerably lower than those of straw

lignin, showing that the chloriting treatment caused considerable demethoxylation. Correction of the total methoxyl in the holocelluloses for the methoxyl in the contaminating lignin yielded values of 0.73% and 0.94% for wheat and oat straws respectively. When computed on the basis of pectin-free straw, these values become 0.58% and 0.72%, as compared with calculated values of 0.56% and 0.60% for wheat and oat straw respectively. The uronic acid content of wheat and oat holocelluloses on recalculation to the basis of straw (pectin-free) showed that no loss occurred in the delignification of the straw.

Isolation of Hemicellulose Fractions from Holocellulose

The preparation of hemicellulose from wood and fibrous plant material is usually carried out with alkali solutions of various strengths. The same method is applicable to holocellulose although prior removal of lignin, to which the hemicelluloses are presumably attached, may affect the solubilities. Of the many fractionations with alkali that have been proposed the method of Wise (27), which gives quantitative recovery, was regarded as most suitable for the present study. The holocellulose fraction was extracted successively with 5% and 24% potassium hydroxide in an atmosphere of nitrogen. The extracted solutions were removed by filtration directly into an excess of glacial acetic acid, the residue was washed with more potassium hydroxide of the same strength and then with water, and the hemicellulose was finally precipitated in the filtrate by the addition of ethanol. The fractions were recovered by centrifuging and finally dried by solvent exchange from ether. The residue, which is arbitrarily termed " α -cellulose", is similar to that obtained by the usual method of extraction of cellulosic material with 17.5% sodium hydroxide. Hemicellulose fractions were soluble in the acetic acid solutions, which had a pH of approximately 4.0, and were precipitated only after the addition of alcohol. This observation indicates that no hemicellulose fraction "A" (Norris and Preece system of separation) was present in wheat and oat straw. Weihe and Phillips (25) found only negligible amounts of this fraction in their study of wheat hemicelluloses. That hemicelluloses appear to have an optimum pH for precipitation was found by Angell and Norris (4) during an investigation of corn cobs. While the hemicelluloses were precipitated by alcohol from acidified solutions in the present study, it appeared worthwhile to investigate the effect of precipitating the fractions from solutions of different pH values. The effects on yield and methoxyl content of the fractions precipitated from solutions of pH 4.0, 5.0, and 6.0 are shown in Table III. The yields at pH 4.0 and 5.0 were quantitative and at pH 6.0 somewhat low. On the basis of the foregoing observations all precipitations were carried out from solutions having a pH of 4.0. The quantitative yields indicate some source of error as yields of 100% are not to be expected since the acetyl groups, which constitute 2 to 3% of the material, are removed by saponification during alkaline extraction. The high results are probably due to difficulty in making an accurate estimation of the ash in hemicelluloses. This difficulty has been discussed by Wise *et al.* (27). As will be shown in the following section there

TABLE III

EFFECT OF pH ON PRECIPITATION OF HEMICELLULOSE FRACTIONS FROM WHEAT STRAW HOLOCELLULOSE

	Residue			Fraction A			Fraction B			Total		
	pH			pH			pH			pH		
	4.0	5.0	6.0	4.0	5.0	6.0	4.0	5.0	6.0	4.0	5.0	6.0
Yield, %	60.3	59.9	58.0	30.2	29.7	29.0	11.3	10.6	8.3	101.8	100.2	95.3
Methoxyl content, %	0.10	0.08	0.12	1.35	1.33	1.36	0.50	0.56	0.53			

was also a loss of methoxyl amounting to about 0.3% of the holocellulose. The methoxyl content of the various fractions was unaffected by the pH of precipitation.

ANALYSIS OF HEMICELLULOSE FRACTIONS AND RESIDUES

Methoxyl Distribution

The yields and methoxyl contents of the hemicellulose fractions isolated from wheat and oat holocelluloses are given in Table IV. The various fractions account for the wheat holocellulose quantitatively; for oat holocellulose the yields are slightly less. Approximately half of the methoxyl groups of the holocelluloses were recovered in fraction A. The over-all recovery of methoxyl was low for both holocelluloses. This observation led to a closer study of the

TABLE IV

METHOXYL CONTENT OF HEMICELLULOSE AND "α-CELLULOSE" RESIDUES OF WHEAT AND OAT STRAW HOLOCELLULOSES

	Fraction A	Fraction B	Residue	Total
<i>Wheat straw holocellulose (Methoxyl content corrected for lignin, 0.73%)</i>				
Yield, %	30.2	11.3	60.3	101.8
Methoxyl, %	1.35	0.51	0.11	
Methoxyl, % (basis of holocellulose)	0.41	0.06	0.07	0.54
Holocellulose methoxyl accounted for in fractions, %	56.2	8.2	9.6	74.0
<i>Oat straw holocellulose (Methoxyl content corrected for lignin, 0.94%)</i>				
Yield, %	30.8	8.45	57.5	96.75
Methoxyl, %	1.43	0.50	0.30	
Methoxyl, % (basis of holocellulose)	0.44	0.04	0.17	0.65
Holocellulose methoxyl accounted for in fractions, %	46.8	4.3	18.2	69.3

methoxyl analysis as applied to the residue portion and to an investigation into the possible types of methoxyl groups in the fractions.

While the modified Viebock and Schwappach method for methoxyl determination gave satisfactory results with straw, holocellulose, and hemicellulose, those with the α -cellulose residues were more difficult to interpret. A small but measurable methoxyl content was found in both wheat and oat residues. The question whether this amount is real or an artifact is raised by the observation of Reeves that an "apparent methoxyl" of 0.2% to 0.3% can be obtained from sucrose, glucose, cellulose, and starch using the Zeisel procedure (17). (There are many modifications of the original Zeisel method; the Viebock and Schwappach method is one of these.) Repetition of Reeves' experiments in this laboratory gave much lower results on sucrose, wheat starch, and purified cotton cellulose. Sucrose gave 0.01% methoxyl after a 50 min. treatment with hydroiodic acid; two additional 50 min. periods yielded a scarcely measurable amount of methoxyl. Starch and cotton yielded about 0.05% methoxyl in a 50 min. treatment; the methoxyl decreased in two further 50 min. periods and became negligible in the fourth and fifth 50-min. treatments. Since the apparent methoxyl contents of the wheat and oat α -cellulose residues were larger than those of purified cotton they are considered to indicate the presence of methoxyl groups. Cooke and Hibberts' trimethylamine method (7) for the isolation of methyl iodide, when applied to the residues, gave a methoxyl value of 0.014% for the wheat holocellulose residue compared with a Zeisel value of 0.114%. Oat holocellulose gave a value of 0.17% by the trimethylamine method as compared with a Zeisel figure of 0.301%. When the trimethylamine methoxyls were used in calculating the balance, the discrepancies between the fractions and the holocelluloses became even greater. Nonetheless it was possible to conclude that the α -cellulose residues contained a small amount of methoxyl. This result is not surprising in view of the fact that α -cellulose and 'true' cellulose of wood and straws are known not to be identical (28). It is interesting to note that the wheat straw α -cellulose prepared from Cross and Bevan cellulose with 17.5% sodium hydroxide contained only 0.07% methoxyl by analysis.

Determination of ester methoxyls by von Fellenberg's method yielded 0.018% and 0.044% for wheat and oat holocellulose respectively. No trace of glycosidic methoxyl was found in either wheat or oat holocellulose by a sensitive method developed by Hoffpauir and Reeves (11). Since the contribution of the ester and glycosidic methoxyls was negligible the conclusion must be reached tentatively that ether methoxyl groups, which are regarded as resistant to alkali, must be partially susceptible to such treatment. In a study of hemicellulosic fractions of aspen holocellulose Thomas was able to account for only 76% of the methoxyl groups although the fractions were quantitatively recovered (24).

Uronic Acid Groups

The determination of uronic acid groups, which occur only in small amounts in cellulosic materials, presents considerable difficulty. It is well

known that pure cellulose, starch, and sugars yield small amounts of carbon dioxide on treatment with 12% hydrochloric acid (5, 15). Anderson states that amounts of carbon dioxide less than 0.3% do not represent the presence of uronic acid (2). Norman (15) and Whistler *et al.* (26) have devised a method of determining uronic acid in the presence of carbohydrates based on the rate of evolution of carbon dioxide. For polyuronides, the rate of evolution is initially high and then falls off progressively as decarboxylation proceeds; for nonuronic carbohydrates the rate is approximately linear with time. However, Nevell (14) has shown that such simple sugars as fructose and sucrose behave as polyuronides.

Uronic acid groups in cotton cellulose of various purities can be fairly readily determined because true cotton cellulose can be used as a control for rate studies of carbon dioxide evolution. However, in straws no such convenient standard exists; the α -cellulose of straws has not been shown to be true cellulose devoid of uronic acid groups. The best that can be done is to use an arbitrary control such as purified cotton cellulose. In the present work the carbon dioxide evolved from purified cotton cellulose under specified experimental conditions was subtracted from the carbon dioxide evolved from the various cellulosic fractions. While this procedure was not ideal it provided the only permissible basis of comparison. The usual conditions of decarboxylation using 12% hydrochloric acid for five hours were compared with those proposed by McCready *et al.* of 19% hydrochloric acid for two hours (13). Using oat holocellulose and purified cotton cellulose the following results were obtained:

Treatment	Yield of carbon dioxide, %		Difference
	Oat holocellulose	Cotton	
12% hydrochloric acid for 5 hr.	1.45	0.28	1.17
19% hydrochloric acid for 2 hr.	1.54	0.39	1.15

The conclusion was reached that the shorter time of decarboxylation was as satisfactory as the longer period. Since Whistler *et al.* (26) have shown that a treatment of five hours with 12% hydrochloric acid was sufficient to determine the uronic acid groups in ramie and flax, the two hour treatment with 19% hydrochloric acid was applied to the cellulosic materials used in the present study. The results of the uronic acid analysis of the hemicellulosic fractions and α -cellulose residues are given in Table V. Almost quantitative recovery of the uronic acid groups was achieved in the various fractions of wheat and oat holocelluloses. About 70% of the uronic acid was contained in Fraction A. This observation supports the general claim that the polyuronides constitute the readily soluble fraction of holocellulose. The small amount of uronic acid in the α -cellulose residues showed that they are not identical with a true cellulose which is composed only of glucose residues.

TABLE V

URONIC ACID ANHYDRIDE CONTENT OF HEMICELLULOSE AND " α -CELLULOSE" RESIDUE OF WHEAT AND OAT HOLOCELLULOSES

	Fraction A	Fraction B	Residue	Total
<i>Wheat straw holocellulose (Uronic acid anhydride content 3.80%)</i>				
Yield, %	30.2	11.3	60.3	101.8
Uronic acid anhydride, %	8.68	5.36	0.80	
Uronic acid anhydride, % (basis of holocellulose)	2.62	0.60	0.48	3.70
Holocellulose uronic acid accounted for in fractions, %	69.0	15.8	12.6	97.4
<i>Oat straw holocellulose (Uronic acid anhydride content 4.32%)</i>				
Yield, %	30.8	8.45	57.5	96.75
Uronic acid anhydride, %	10.20	6.40	0.76	
Uronic acid anhydride, % (basis of holocellulose)	3.14	0.54	0.44	4.12
Holocellulose uronic acid accounted for in fractions, %	72.7	12.5	10.2	95.4

Molar Ratio of Uronic Acid Anhydride to Methoxyl Groups

The molar ratio of uronic acid anhydride to methoxyl groups in holocellulose, hemicellulose A and B, and the α -cellulose residues of wheat and oat holocelluloses are given in Table VI. For the holocelluloses, the molar ratios were

TABLE VI

MOLAR RATIO $\frac{\text{URONIC ACID ANHYDRIDE}}{\text{METHOXYL}}$ IN WHEAT AND OAT HOLOCELLULOSES AND THEIR HEMICELLULOSE FRACTIONS

	Wheat	Oat
Holocellulose	0.92	0.82
Fraction "A"	1.33	1.07
Fraction "B"	2.20	1.54
" α -Cellulose" residue	1.10	0.47

less than unity. A value of 1.29 can be calculated from data published by Schenck and Kurth for wheat straw holocellulose (21); a similar calculation applied to data reported by Thomas for aspen holocellulose yields a molar ratio of 1.07 (24). The proximity of these values to 1 suggests the presence of hexuronic acid groups containing one methoxyl. In fractions A and B the molar ratio was greater than unity. The relatively high ratio in fraction B indicates that some uronic acid residues may not contain a methoxyl group. The uncertainty of the analytical methods, especially for methoxyl as applied

to the residues, makes calculations of the ratios of doubtful value. The possibility cannot be overlooked that some of the uronic acid in the residues may have been formed by oxidation during the fractionation procedures. A hemicellulose fraction extracted from white birch by ethylenediamine has been reported by Sitch (22) to contain a $\frac{\text{uronic acid}}{\text{methoxyl}}$ molar ratio of 1.6. Various hemicellulosic fractions isolated by Sands and Nutter (20) from mesquite wood contained a $\frac{\text{methoxyl}}{\text{uronic}}$ ratio of 1.0. While most investigators have presumed that the methoxyl group is attached to the uronic acid residue, a report by Anderson and Kinsman on the isolation and identification of an aldobionic acid from cottonseed hulls does not mention methoxyl groups being found in the isolated glucuronic acid portion (3).

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SEPARATION OF P^{32} FROM NEUTRON-IRRADIATED SULPHUR¹

By A. H. BOOTH

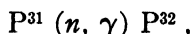
Abstract

A method for extracting P^{32} from neutron-irradiated sulphur has been developed. The sulphur is melted under a mixture of acetic acid and acetic anhydride at boiling temperature, and the P^{32} is recovered from the residue left after distilling the acid. An apparatus for carrying out the process by remote control is described. It has been used for production of 100 millicurie amounts of carrier-free P^{32} at the Chalk River laboratories.

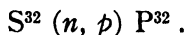
Introduction

P^{32} is one of the more commonly used radioisotopes in tracer work, and preparations having high activity and high specific activity are frequently required. The method described below has been used for separation and purification of 100 millicurie amounts.

In the nuclear reactor or "pile", P^{32} can be synthesized by two methods. The direct irradiation of phosphorus with slow neutrons,

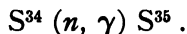


gives a high yield, but the specific activity attainable by the method is limited. A much greater specific activity is given by irradiation of sulphur with fast neutrons,



The P^{32} can then be separated chemically from the parent sulphur.

Elemental sulphur is the most suitable target material. It is thermally stable and easily obtained free from objectionable impurities. Undesirable side reactions are thus minimized; the only other important radioactive product is S^{35} formed by the reaction,



The phosphorus atoms, when formed, are locked inside the sulphur crystal lattice, and no separation can be made until the crystal structure is broken by melting or solution. Because of its minute concentration the phosphorus may then react very quickly with trace impurities, particularly oxygen. Until complete oxidation has been ensured the possible coexistence of several valence states must be considered.

Separation can be made by several methods, but when highly active material is processed the simplicity of the method chosen is of prime importance. Manipulations must be carried out from behind a shield sufficiently thick to protect the operator from the high energy beta rays. Consequently, each

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operation must be adaptable to remote control. A high yield is secondary to this consideration.

Preliminary experiments by others (2) in this laboratory indicated that good separation could be made either by dissolving the sulphur in carbon disulphide and extracting the P^{32} with dilute nitric acid, or by leaching the molten sulphur with superheated water in a pressure vessel. These methods presented some difficulties and hazards in remote control operation. Cohn (1) has described a method for extracting P^{32} with concentrated nitric acid. The constant boiling temperature of the acid is just high enough to keep the sulphur molten during extraction. This procedure also is difficult to adapt to remote control because the sulphur must be melted separately and poured slowly into the boiling acid. Furthermore a considerable amount of sulphuric acid is formed, and the S^{35} introduced into the solution can cause some difficulty in subsequent steps.

Experimental

Extraction of P^{32} by Organic Liquids

Extraction with a liquid at ordinary pressure is one of the less difficult operations to adapt to remote control. For this reason a number of organic liquids with boiling points in the range 120° to 150° C. were examined as possible extracting agents. The case of acetic acid is somewhat exceptional in that its boiling point, 118° C., is slightly less than the melting temperature of sulphur. There is ordinarily enough superheat at the wall of the flask to overcome this, and the melted sulphur then can be dispersed readily because it does not resolidify until the temperature falls below 112° C. Occasional failures were noted, and it was found necessary to raise the boiling point somewhat by adding acetic anhydride.

Yield tests were carried out as follows. Neutron-irradiated sulphur was heated with the solvent under reflux until melted. The solvent was boiled for 15 min. while the sulphur was agitated with a current of air. After cooling, the solvent was decanted, and its P^{32} content determined using a conventional type of Geiger counter (3). A 25 mgm. per cm^2 aluminum absorber was placed between sample and counter tube to eliminate any radiation due to S^{35} activity. The sulphur residue was oxidized to sulphuric acid with a mixture of nitric acid and bromine and then tested in the same way.

Some results are shown in Table I. Acetic acid gave a much higher yield than the nonpolar solvents. With successive extractions a maximum value was soon reached, the nonextractable portion presumably being combined with impurities such as iron. The greater efficiency of the acid solvents may be explained by a tendency to dissociate such compounds. Excessive iron or aluminum impurity lowers the yield, but variation of iron content in the range 25 to 100 p.p.m. has no appreciable effect. The values given refer to a technical grade roll sulphur containing about 25 p.p.m. of iron.

The mechanism of the extraction was not determined but it is unlikely that elemental phosphorus is involved. More probably the phosphorus reacts

TABLE I

YIELDS OF P^{32} EXTRACTED FROM NEUTRON-IRRADIATED SULPHUR BY ORGANIC LIQUIDS

Extracting liquid	Vol., ml./gm. of sulphur	P^{32} extracted, %		
		One extraction	Two extractions	Three extractions
Glacial acetic acid	5	83	90	92
Acetic acid – acetic anhydride mixture 3 : 1 by vol.	2	70	85	88
	5	80	87	89
	10	81	88	90
Propionic acid	5	57	69	—
Isoamyl acetate	5	56	58	—
Isoamyl alcohol	5	58	59	—
Diisopropyl ketone	5	55	57	—

first with traces of oxygen and water and is taken into solution as phosphorous and phosphoric acids. Evidence to support this view is the fact that nearly all the P^{32} remains in the nonvolatile residue when the sulphur is sublimed in air.

Distillation, Recovery, and Purification

Acetic acid and the acetic acid – acetic anhydride mixture were selected for further study. When the extract is decanted from the sulphur and distilled, all the P^{32} remains in the residue. This residue is chiefly sulphur carried over in solution. The solubility of sulphur in glacial acetic acid is about 1 gm. per 100 ml. at boiling, and about 0.05 gm. per 100 ml. at room temperature. On cooling, the dissolved sulphur separates in large crystals from which the solution can easily be decanted. The distillation is carried out at a low temperature in the final stages to prevent the formation of plastic sulphur.

The P^{32} can be leached from the residue by boiling with dilute mineral acid. The percentage recovered depends on the amount of residue and conditions of distillation, but is always high, provided the residue has not been overheated. Under the conditions described later recoveries of 90% to 96% were obtained.

In the resulting solution the P^{32} is present as orthophosphate ion only. Meta and pyrophosphates formed in the residue would be hydrolyzed to orthophosphate during the boiling leach. Phosphites were shown to be absent by adding sodium phosphite carrier and reducing with zinc in hydrochloric acid. The evolved phosphine contained negligible P^{32} activity.

At this point the solution contains no sulphur or sulphuric acid, but trace impurities such as iron and organic matter are sometimes present. The purification procedure described by Cohn (1) gave good results. The phosphate is precipitated by ammonia on ferric or lanthanum hydroxide carrier. A basic phosphate is formed which coprecipitates with the hydroxide. Sodium or potassium hydroxide cannot be used as precipitant because the basic

phosphate is then not formed. Subsequently, cations are removed by dissolving the hydroxide in hydrochloric acid and passing the solution through a base-exchange resin. The resin used in this work was Dowex-50. It was conditioned before use by three or four sodium-hydrogen exchange cycles, ending finally in the hydrogen form.

Remote Control Apparatus

The procedure outlined above is readily adapted to remote control. The apparatus used in some experimental runs is shown in Fig. 1. It is enclosed behind a $\frac{3}{8}$ in. screen of "Lucite" sheet, and operated entirely by remote control. Since no gamma rays are emitted this shield provides adequate

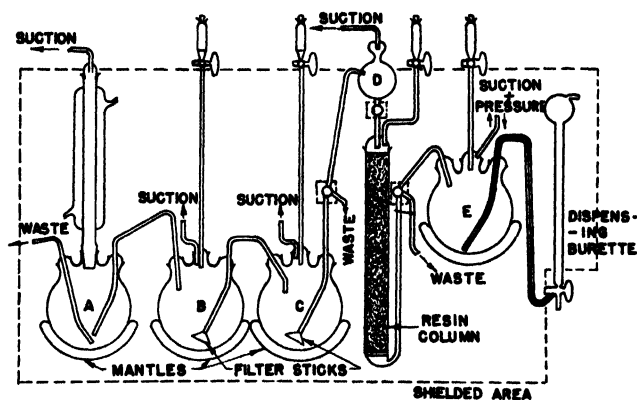


FIG. 1. Remote control apparatus for P^{32} extraction.

protection. The three stopcocks indicated by the dotted squares are controlled by rods extending through the shield, but all other valves are accessible directly. Suction and pressure lines are brought together on stopcock manifolds mounted on a control panel.

From 20 to 100 gm. of sulphur is introduced into *A* through the condenser and a 3 : 1 mixture of acetic acid and acetic anhydride added in an amount corresponding to 2 to 5 ml. per gm. of sulphur. The condenser cap is replaced and the mixture heated. When the sulphur has melted under the boiling liquid it is agitated for about 30 min. by a stream of air drawn through the siphon tubes. The air stream is maintained during cooling so that the ends of the siphon tubes do not become sealed.

Two extractions are made and the extracts combined in *B*, then distilled back into *A*, using slight vacuum in the receiver. About 100 ml. of 0.1 *N* hydrochloric acid is run in to *B*, boiled for five minutes and drawn over into *C* through the filter stick.

The hydroxide precipitation is carried out in *C*. Four milligrams of ferric chloride is added and precipitated with 20 to 25 ml. of 1.0 *N* ammonia. The solution is boiled, cooled somewhat, and the supernatant drawn over into a waste flask through the filter stick. The precipitate is washed with water, then redissolved in 100 ml. of hot 0.05 *N* hydrochloric acid, drawn up

into *D*, and passed through the resin column. The outlet tube of the column is bent up into a position only a few inches below the top of the column packing, so that the column cannot run dry inadvertently.

The effluent is dispensed directly as carrier-free P^{32} in acid solution, or it is evaporated to dryness in *D* and taken up in neutral solution. In the second case addition of a small amount of inactive phosphate is necessary to prevent adsorption on the walls of the container.

The waste sulphur is remelted under acetic anhydride and drawn over quickly into a disposable flask outside the shield. Liquid wastes in holding flasks (not shown) are run to drain, the siphon being started with a pressure bulb. Flask *B* is cleaned periodically with concentrated sulphuric acid.

Discussion

An apparatus similar to that described has been operated for some months at Chalk River. The arrangement is compact and the entire procedure can be carried out in a few hours. Activities greater than 100 millicuries have been separated without difficulty.

Modifications in technique are still being made and under the changing conditions over-all yields have varied from 50 to 80%. Some loss occurs in each stage, because, at this minute concentration of phosphate, it is difficult to prevent entirely an irregular adsorption on the apparatus and column filling. If a few milligrams of inactive phosphate are added early in the process, losses are minimized, but this, of course, lowers the specific activity of the product. In general, yields decrease with increasing size of batch treated. This can probably be accounted for by less efficient agitation, larger distillation residue, and greater total quantity of impurities introduced. The method in its present form is limited, therefore, to amounts of sulphur less than 150 gm. The availability at Chalk River of high neutron fluxes makes targets of this size entirely adequate.

Acknowledgments

The author wishes to express his thanks to Mr. G. P. Maxwell, who carried out some of the high activity runs, and to Mr. N. L. F. Jupe for assistance in the experimental work.

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1,10-PHENANTHROLINE, 2,2'-BIPYRIDYL, AND THE PLATINUM METALS¹

By D. E. RYAN²

Abstract

A previously described method for the determination of palladium with 1,10-phenanthroline is herein further extended and investigated. In all cases the complex is used as the weighing form for palladium, the theoretical factor 0.2982 being used to calculate the palladium content. The reactions of palladium, platinum, iridium, rhodium, and gold with 1,10-phenanthroline and 2,2-bipyridyl are described. Palladium may be separated from rhodium by a single precipitation, using 1,10-phenanthroline as precipitant. A double precipitation enables palladium to be separated from platinum and iridium.

Introduction

The use of compounds containing the active functional group $\text{N}=\text{C}=\text{C}=\text{N}$, to which 2,2'-bipyridyl and 1,10-phenanthroline owe their capacity to react, as precipitants for certain cations and anions has not been studied extensively. DeVries (1) reported the separation and microdetermination of ferrous iron and determined perchlorates, periodates, and persulphates in the presence of chlorate, iodate, and sulphate, using 5-nitro-1,10-phenanthroline ferrous sulphate as precipitant. Gillis (2) studied the reactions of ferroin with different anions in water and in hydrofluoric acid medium, and Ryan and Fainer (3) used 1,10-phenanthroline to precipitate palladium from palladous chloride solutions. The following report is the result of further investigation into the use of these reagents for platinum metal determination.

Experimental and Results

Reagents

- 1,10-Phenanthroline: 0.5 gm. of 1,10-phenanthroline dissolved in 100 ml. of water.
- 2,2'-Bipyridyl: 0.5 gm. of 2,2'-bipyridyl dissolved in 100 ml. of water.
- Palladous chloride solutions—prepared by dissolving $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ in 0.5 *M* hydrochloric acid solution and standardized by the dimethylglyoxime method.
- Palladous nitrate, palladous sulphate, platinic chloride, rhodium chloride, iridium tetrachloride, and gold chloride solutions—prepared from the metal or suitable pure salt and containing approximately 1 mgm. of the metal per ml. of solution.

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Reactions of Palladous Salts with 1,10-Phenanthroline and 2,2'-Bipyridyl

1,10-Phenanthroline and 2,2'-bipyridyl react with palladous salts to give complexes of the type $\text{PdC}_{12}\text{H}_8\text{N}_2\text{Cl}_2$. The complex formed with 1,10-phenanthroline is a pale yellow solid, while that with 2,2'-bipyridyl is a brighter yellow. The 1,10-phenanthroline complex is very insoluble, while that with 2,2'-bipyridyl is slightly soluble in water. Palladous nitrate gives with 1,10-phenanthroline a fine crystalline yellow precipitate that has a similar composition, $\text{PdC}_{12}\text{H}_8\text{N}_2(\text{NO}_3)_2$. The dry compound is slightly soluble in cold but appreciably soluble in hot water. Palladous sulphate gives no precipitate on the addition of 1,10-phenanthroline, but a flocculent precipitate forms immediately on the addition of chloride to this solution. On the addition of halides other than chloride to a solution of 1,10-phenanthroline and palladous sulphate, the following results are obtained: fluoride gives a white gelatinous precipitate, bromide gives a yellow flocculent precipitate, and iodide gives a heavy brown precipitate. The composition of these precipitates has not been investigated.

Reactions of Platinum, Rhodium, Iridium, and Gold with 1,10-Phenanthroline and 2,2'-Bipyridyl

In a previous paper (3) it was reported that no precipitates were obtained with platinum, rhodium, and iridium, using 1,10-phenanthroline. The conditions used in obtaining these results involved dilute solutions (0.05 mgm. of Pt metal per ml. of solution) that were maintained near the boiling point for two hours. Further investigation shows that, in more concentrated solutions, precipitates are obtained from platinum (PtCl_6^-) and iridium (IrCl_6^-) solutions. The platinum precipitate is orange yellow, while the iridium precipitate is reddish brown. Precipitation is incomplete, with little precipitate being obtained in dilute solutions. Rhodium gives no precipitate even from concentrated solution. 2,2'-Bipyridyl reacts similarly to 1,10-phenanthroline.

Gold is precipitated, as a complex, from hydrochloric acid solutions. This canary yellow precipitate dissolves on heating. Since no yellow color was noted in the filtrate from the precipitation of gold (in the cold), a series of tests was carried out to determine if the precipitation is complete. Using 2,2'-bipyridyl as precipitant, incomplete precipitation was found in all cases where hydrochloric acid concentration was varied from 1 to 20%. Similar results were obtained using 1,10-phenanthroline. The stannous chloride spot test was used to test for completeness of precipitation.

The Determination of Palladium with 1,10-Phenanthroline and 2,2'-Bipyridyl

The procedure for the determination of palladium with 1,10-phenanthroline was essentially that previously described (3). Since, however, the composition of the complex is constant and has a low palladium content, all results unless otherwise indicated were obtained using $\text{PdC}_{12}\text{H}_8\text{N}_2\text{Cl}_2$ as the weighing form for palladium. Samples of the standard palladous chloride solution were measured into 250 ml. beakers, the volume made up to approximately 150 ml.,

and the palladium precipitated with 1,10-phenanthroline. These solutions were allowed to stand for two hours, and the precipitates were filtered through medium porous porcelain crucibles, washed with 1% hydrochloric acid, dried at 110° C., and weighed as the complex. The results obtained by this procedure are shown in Table I. The quantity of palladium was calculated, using the theoretical factor 0.2982.

TABLE I
DETERMINATION OF PALLADIUM WITH 1,10-PHENANTHROLINE,
WEIGHING AS $\text{PdC}_{12}\text{H}_8\text{N}_2\text{Cl}_2$

No.	Palladium taken, mgm.	Palladium recovered, mgm.
1	11.04	11.05
2	11.04	11.01
3	11.04	11.03
4	11.04	11.03
5	11.04	11.06
6	11.04	11.03
7	11.04	11.00
8	11.04	11.03
9	10.86	10.86
10	10.86	10.89
11	10.86	10.86

The results obtained by a similar procedure with 2,2'-bipyridyl are shown in Table II. These results were obtained using $\text{PdC}_{10}\text{H}_8\text{N}_2\text{Cl}_2$ as the weighing form and the theoretical factor 0.3124.

TABLE II
DETERMINATION OF PALLADIUM WITH 2,2'-BIPYRIDYL

No.	Palladium taken, mgm.	Palladium recovered, mgm.	Volume solution, ml.
12	10.86	10.88	50
13	10.86	10.86	75
14	10.86	10.84	100
15	10.86	10.48	200
16	10.86	10.10	300
17	10.86	9.01	400

Table II shows the effect of concentration on the degree of precipitation, using 2,2'-bipyridyl as precipitant. Similar experiments with 1,10-phenanthroline showed no such deviations, complete precipitation being obtained in all cases. When 10.86 mgm. of palladium was taken the palladium recovered from 400 ml. of solution, using 1,10-phenanthroline, weighed 10.86 mgm. A second sample weighed 10.87 mgm.

The Precipitation of Palladium from Solutions Containing Other Platinum Metals

Since dilute solutions of platinum metals other than palladium gave only slight precipitates with 1,10-phenanthroline, attempts were made to separate palladium from platinum, iridium, and rhodium.

The palladium was precipitated as previously described from solutions "salted" with varying amounts of the other metals. Results 18 to 21 in Table III show that palladium may be separated from rhodium by a single precipitation. Results 22 to 25, obtained in the presence of iridium and platinum, are approximately 2% high.

TABLE III

DETERMINATION OF PALLADIUM IN PRESENCE OF OTHER PLATINUM METALS

No.	Palladium taken, mgm.	Palladium recovered, mgm.	Platinum metal added, mgm.
18	11.04	11.01	5 Rh
19	11.04	11.00	5 Rh
20	11.04	11.00	5 Rh
21	11.04	11.03	10 Rh
22	11.04	11.10	3 Ir
23	11.04	11.16	6 Ir
24	10.86	11.02	6 Pt
25	10.86	11.05	6 Pt
26	10.84	10.81	10 Pt
27	10.84	10.83	10 Pt
28	10.84	10.78	10 Pt
29	4.77	4.72	20 Pt
30	4.77	4.73	6 Ir
31	4.77	4.72	6 Ir

Reprecipitation Method

Since high results were obtained by a single precipitation when platinum and iridium were present, a double precipitation was attempted. The precipitate was filtered through retentive filter paper, and nitric and sulphuric acids were used to destroy organic matter. The solution was evaporated to sulphuric acid fumes, diluted with 1% hydrochloric acid after filtration and the palladium reprecipitated. The precipitate was very yellow and the results obtained, the precipitate being weighed as $\text{PdC}_{12}\text{H}_8\text{N}_2\text{Cl}_2$, were 5% high. It was subsequently discovered that the procedure using nitric and sulphuric acids resulted in nitration of the 1,10-phenanthroline, with incomplete destruction of the organic matter.

Although satisfactory results should be obtained on ignition of the above precipitate and weighing as the metal, an alternative procedure was used that allows use of $\text{PdC}_{12}\text{H}_8\text{N}_2\text{Cl}_2$ as the weighing form. The samples, after the first precipitation, were filtered through ashless filter paper and ignited over a burner. These residues were transferred to conical flasks, which were

closed with short-stemmed funnels, and dissolved in aqua regia. The solutions were evaporated several times in the presence of excess hydrochloric acid, filtered, diluted, and the precipitation carried out as previously described. Results 26-31 in Table III show that palladium may be separated from platinum and iridium by this method. Attempts to separate palladium from gold by the same procedure were unsuccessful.

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THE THERMAL DECOMPOSITION OF CUMENE HYDROPEROXIDE IN RELATION TO CERTAIN ASPECTS OF EMULSION COPOLYMERIZATION¹

BY J. W. L. FORDHAM AND H. LEVERNE WILLIAMS

Abstract

Cumene hydroperoxide decomposes near 100° C. in reactive solvents but only slightly in stable solvents. The decomposition is not a simple first order reaction. The results may be interpreted as the sum of a first and a three-halves order reaction. Approximate over-all energies of activation of the decomposition determined from the data obtained for the decomposition in cumene (31 kcal. per mole), methanol (31 kcal. per mole), styrene (20 kcal. per mole), and the energy of activation for the initial unimolecular step in benzene-styrene mixtures (30.4 kcal. per mole) agree with the values reported for similar peroxides and hydroperoxides in similar solvents. The energy of activation for the radical-induced decomposition is 6.5 kcal. per mole. The data suggest that the first step of the decomposition is the unimolecular reaction involving scission of the O-O bond. If the resultant $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O}^\bullet$ radical is not reactive towards the solvent, it tends to lose either a phenyl or a methyl radical and form acetone or acetophenone respectively. The former reaction predominates. The decomposition rapidly becomes autocatalytic, particularly in cumene at higher temperatures, presumably because of the radical-induced decomposition of the hydroperoxide. The identified products of decomposition in cumene can be explained by the various reactions of the radicals formed in the mixture. The polymerization shortstop 2,5-ditertiarybutylhydroquinone reacts rapidly below 0° C. with an equimolar weight of cumene hydroperoxide, and the resulting products retard further thermal decomposition at 90° C. quite strongly. The shortstop 2,4-dinitrochlorobenzene does not react with cumene hydroperoxide and would seem to act merely as a powerful retarder for the decomposition at the higher temperature. The effect of other related compounds on the decomposition of cumene hydroperoxide in styrene was less marked and agrees with the relatively less effectiveness of these compounds as stoppers in emulsion copolymerization.

Introduction

Organic peroxides and hydroperoxides are initiators of free-radical-induced polymerization reactions. Hence a knowledge of the mechanism of their decomposition is becoming important in this field. Hydroperoxides are present as intermediate compounds in the oxidation of hydrocarbons, including hydrocarbon polymers. Their decomposition plays a role in the degradation of these polymers and in the drying of oils. Considerable research has been carried out on the decomposition of peroxides, but as yet there is very little pertinent data available on hydroperoxides such as cumene hydroperoxide, which is used currently as an initiator in the low temperature butadiene-styrene copolymerization recipes (17, 21). Consequently a preliminary study of the decomposition of this compound as related to polymerization initiation and stopping was undertaken. The results obtained in the thermal decomposition are presented in this report. No similar published data for this compound have been found.

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Contribution from the Research and Development Division, Polymer Corporation Limited, Sarnia, Ont. Presented in part before the Physical Chemistry Division, Chemical Institute of Canada, Halifax, May, 1949.

The literature revealed that certain types of reactions are common to the decomposition of peroxides and hydroperoxides in solvents. The initial scission is accepted to be at the central O-O bond. If the radical that is formed contains the -COO- group there is a marked tendency for carbon dioxide to be split off, leaving a new radical (7, 13), particularly when the initial radical does not react readily with the solvent molecule (13) or when the temperature is increased (14). However, if the initial radical contains the -CO- group, there is a tendency for C-C fission to take place at the weakest adjacent bond of the α -carbon atoms to yield a ketone or aldehyde (9, 20, 26, 27) especially when the temperature is increased (20). This reaction is thermodynamically possible because the energy required to split the C-C bond is balanced by that released in the formation of the C=O bond from the C-O bond. Both the initial radical and the resultant radical produced by it can abstract an α -hydrogen atom from the solvent if this atom is available (5, 6, 13, 14, 15, 20). These radicals attack olefin molecules at the α -carbon atoms and at the double bond (7), thereby initiating polymerization. Then to stop polymerization at the desired degree of conversion of hydrocarbons to rubber some agent must be added to inactivate the free radicals present and prevent the formation of further free radicals.

It would be desirable but very difficult to study the decomposition of cumene hydroperoxide under conditions present during emulsion copolymerization. However, the mechanism of emulsion polymerization is considered to be the same as of bulk polymerization (8). Hence it is a great simplification to study those reactions known to take place in the oil phase by comparatively simple solution techniques and apply the results to the emulsion system, allowance being made for the influence of aqueous phase. For this reason the thermal decomposition of cumene hydroperoxide was studied in hydrocarbon solutions. Since all the hydrocarbons are slightly soluble in water and are solubilized and dispersed by the emulsifying agents, some refinement of the results will be required in applying them to the emulsion system.

Methods

Analysis for Cumene Hydroperoxide

Of the methods of analysis for peroxides and hydroperoxides disclosed in the literature (1, 18, 22, 23, 24) the iodometric method, which yields precise results from a simple procedure, seemed the most desirable to adopt for cumene hydroperoxide. Nozaki's modification of this method was tested first. The results depended upon the reaction time between sodium iodide and cumene hydroperoxide in acetic anhydride medium both at room temperature and at a higher temperature obtained by placing the flask on a hot plate set at low heat. This method also has the disadvantage that individual portions of sodium iodide must be weighed for each analysis. A stock solution of sodium iodide in acetic anhydride cannot be made because the iodide is oxidized continually to iodine by the atmospheric oxygen, the supply of which is renewed every time that the solution is exposed to the atmosphere.

Because of these disadvantages the method suggested by the Hercules Powder Company* was tested. In this method the sample is added to 100 ml. of 99% isopropanol in a glass-stoppered Erlenmeyer. Ten milliliters of glacial acetic acid and 1 ml. of saturated potassium iodide solution are added and the mixture is refluxed gently (to avoid the loss of iodine) for three to four minutes. The condenser is washed with 10 ml. of isopropanol, 25 ml. of water is added, and the flask stoppered. When the resulting solution has cooled somewhat, the liberated iodine is titrated with standard thiosulphate solution to the disappearance of the yellow color. Starch cannot be used as an indicator, but this is not a serious disadvantage unless the solution is objectionably colored. A blank is measured on the reagents. This procedure is somewhat simpler than the previous one and gives reproducible results that are independent of the time of refluxing up to 10 min. and gives only very small errors up to 25 min. refluxing. It was the method chosen for the subsequent investigation.

Purification of the Cumene Hydroperoxide

Commercial cumene hydroperoxide supplied by the Hercules Powder Company assayed approximately 70% active material and was purified by the method used by that Company*. One hundred milliliters of the crude hydroperoxide was slowly added to 300 ml. of a 25% sodium hydroxide solution in water. The mixture was agitated well and cooled to maintain the temperature below 30° C. Crystals of the sodium salt were formed and were filtered from the caustic solution. The filtered crystals were washed twice with 25 ml. portions of benzene and then stirred in 100 ml. of benzene for 20 min. The sodium salt was filtered and the washing operation repeated, using 100 ml. of fresh benzene. The sodium salt was filtered once more, washed with two more 25 ml. portions of benzene, and suspended in 100 ml. of distilled water. The pH was lowered to 7.5 with 4 *N* hydrochloric acid, the hydroperoxide extracted twice, using 20 ml. portions of *n*-pentane. The moisture and solvent were removed under vacuum at room temperature and the last traces were removed at 1 mm. pressure and 40° to 50° C. The recovery was 85% to 90% of a material that ranged in purity from 97% to 100% active hydroperoxide.

Decomposition of Cumene Hydroperoxide in Solvents

The solvent was subjected to a distillation at atmospheric pressure (except styrene, which was distilled at 1 mm. pressure to prevent polymerization) in order to remove any dissolved oxygen from the solvents, and any inhibitor from the styrene and the middle third was collected. Unless otherwise stated a 2% by weight solution of 98% cumene hydroperoxide was made, using the freshly distilled solvent. A definite volume of the solution was transferred to each reaction tube by means of a pipette. The reaction tubes consisted of 12-in. lengths of 9 mm. glass tubing that had been rinsed previously with distilled water, dried, and sealed off at one end. The tubes containing

* *Private communication.*

Source of Chemicals

Solvent	Source	Grade	Purification	$\eta \frac{25}{D}$
Cumene	Polymer Corp. Ltd.	Mixture of alkylated benzenes	Fractionated at atmospheric pressure in a 65 plate Stedman column at a 10 : 1 reflux ratio	1.4887
Methanol	E. I. du Pont de Nemours	Synthetic	Same. Dried over potassium carbonate	1.3275
Styrene	Polymer Corp. Ltd.	Technical	None	1.5438
Benzene	Algoma Steel Co.	Technical	Fractionated at atmospheric pressure in a 65 plate Stedman column at a 10 : 1 reflux ratio	1.4980
n-Hexane	Phillips Pet. Co.	Technical	None	1.3729
2,5-Ditertiarybutyl-hydroquinone	Eastman Kodak Co.	Practical	Recrystallized from benzene	—
2,5-Ditertiarybutyl-hydroquinone	Monsanto	Recrystallized	None	—
2,4-Dinitrochlorobenzene	Eastman Kodak Co.	Pure	Recrystallized from benzene	—
2,6-Ditertiarybutyl-4-methylphenol	Standard Oil Co.	Deenax	Recrystallized from benzene	—
Phenyl- β -naphthylamine	Canadian Industries Ltd.	Neozene D	Recrystallized three times from methanol	—

the peroxide solution were immersed in a dry ice - ethanol bath. In groups of four these were evacuated, flushed with commercial nitrogen, evacuated, flushed, evacuated, and sealed off under vacuum in succession, so that they contained approximately the same vapor volume above the solution and were approximately 10 in. in length. The tubes were transferred from the dry ice - ethanol bath to a constant temperature ethylene glycol bath maintained within one-tenth of a centigrade degree. Each tube was left in the bath for the desired reaction time and then quenched in the dry ice - ethanol bath. The tube was opened and the residual hydroperoxide was determined iodometrically, using the procedure of the Hercules Powder Company as outlined previously, with the modification that 10 ml. of the isopropanol was held back from the titration flask in order to rinse the reaction tube. In the later studies the reaction tube was rinsed with 10 ml. of toluene before the alcohol to ensure complete removal of the sample. The undecomposed sample for every series of results was analyzed to check the strength of the original solution, and this was taken as the initial concentration.

Results

Decomposition of Cumene Hydroperoxide in Single Solvents

The results for the thermal decomposition at 90.5°, 99.7°, and 109.4° C. of a 2% solution of cumene hydroperoxide in cumene, methanol, and styrene as representative solvents are given in Figs. 1 to 3 respectively. The accuracy

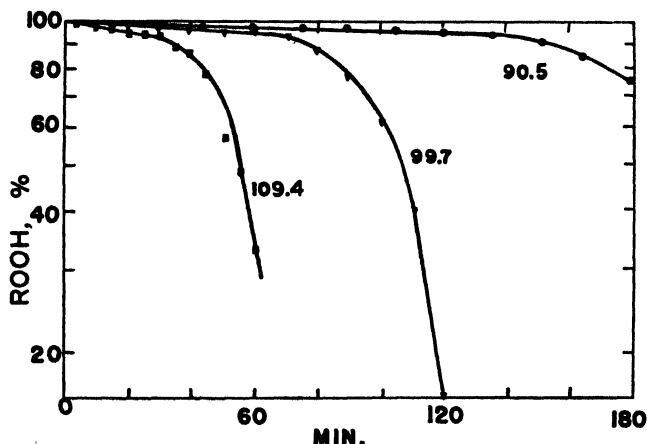


FIG. 1. Per cent residual cumene hydroperoxide versus time at 90.5, 99.7, and 109.4° C. in cumene.

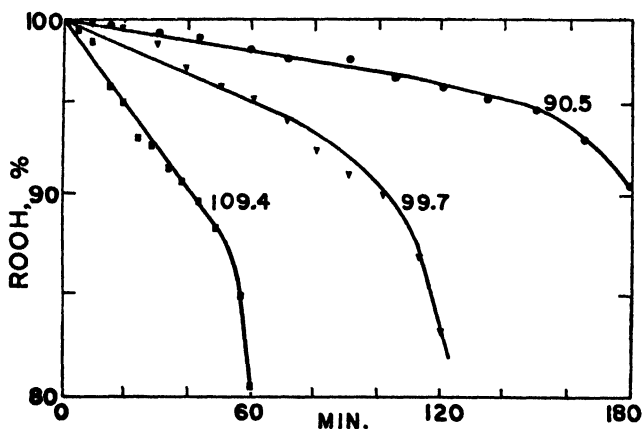


FIG. 2. Per cent residual cumene hydroperoxide versus time at 90.5, 99.7, and 109.4° C. in methanol.

of the results obtained after considerable polystyrene had formed was decreased because the high viscosity of the solution made it difficult to remove the entire sample. The graph of the logarithm of the unreacted cumene hydroperoxide against time shows that the peroxide disappears initially much more rapidly in styrene than in either cumene or methanol in which the rates are approximately equal. The decomposition appears to be autocatalytic in all cases and this effect is much more pronounced in cumene. In the latter case the final rate of disappearance is the fastest of all those measured. The autocatalytic effect is greater at the higher temperatures.

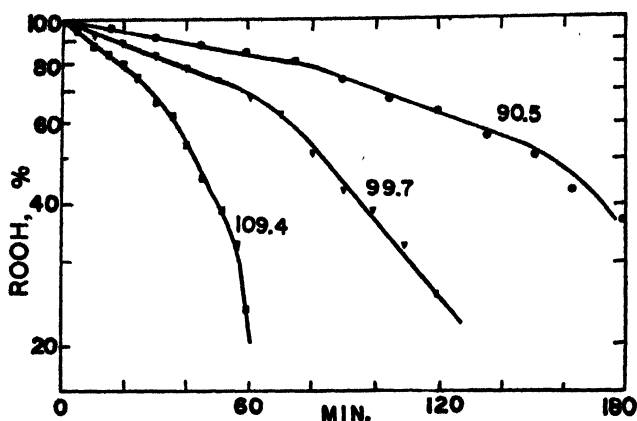


FIG. 3. Per cent residual cumene hydroperoxide versus time at 90.5, 99.7, and 109.4° C. in styrene.

The decomposition is not first order but if the graphs are assumed linear during the first few per cent decomposition then rate constants can be calculated from large scale graphs. The data are in Table I. Approximate

TABLE I

EFFECT OF TEMPERATURE ON RATE CONSTANTS IN VARIOUS SOLVENTS

T° A	Cumene	Methanol	Styrene
363.7	$2.1 \times 10^{-4} \text{ min.}^{-1}$	$2.9 \times 10^{-4} \text{ min.}^{-1}$	$3.05 \times 10^{-3} \text{ min.}^{-1}$
373.9	6.0	8.2	6.25
382.6	18	24	11.90

activation energies calculated from these data yield a value of 31 kcal. per mol. for the decomposition in cumene or methanol and 20 kcal. per mol. in styrene as solvent. These values are in good agreement with those reported for similar peroxides and hydroperoxides in similar solvents (3, 10, 16, 25).

Repetition of the work at 90.5° C., using two initial concentrations of cumene hydroperoxide (1% and 2%), yielded the data in Fig. 4. Calculation of the first order rate constants for disappearance gave the results in Table II. The variation of the constants with concentration even over this narrow range suggest further that the reaction is not first order.

TABLE II

EFFECT OF CONCENTRATION ON RATE CONSTANT IN VARIOUS SOLVENTS

Solvent	2% Cumene hydroperoxide	1% Cumene hydroperoxide
Cumene	$2.2 \times 10^{-4} \text{ min.}^{-1}$	$2.1 \times 10^{-4} \text{ min.}^{-1}$
Methanol	1.5	1.2
Styrene	30.5	26.5

Comparison of the data in Tables I and II and Figs. 2 and 4 will show that in Table II and Fig. 4 the rate of disappearance in methanol has diminished with the use of a new distillation batch from the same can of the solvent. This

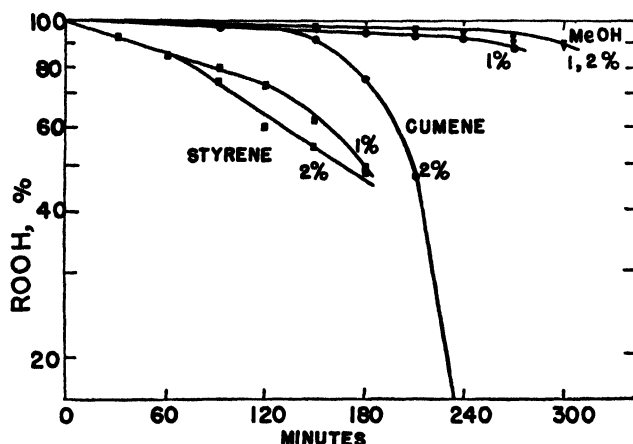


FIG. 4. Per cent residual cumene hydroperoxide versus time at 90.5° C. for two initial concentrations of hydroperoxide.

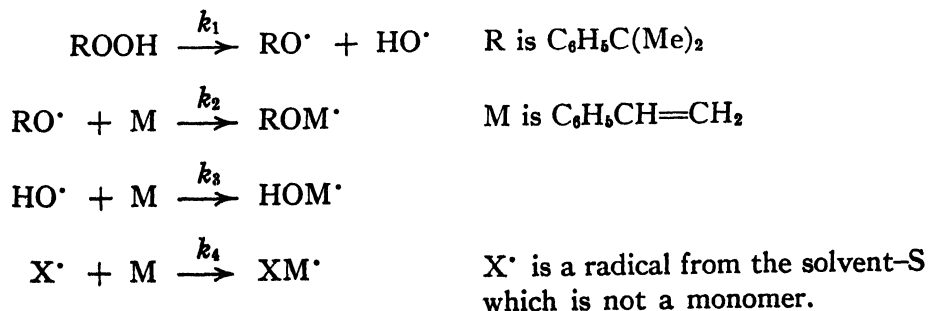
emphasizes the need for uniform batches of materials in these studies. It will be noted too that the autocatalytic effect in cumene is not as evident with the lower concentration of cumene hydroperoxide. Otherwise the agreement between these two series of data is good.

When benzene was used as solvent 91.2% of the hydroperoxide remained after 414 min. at 109.4° C. whereas there was no decomposition in *n*-hexane in three hours at 109.4° C. Evidently the decomposition is much slower in solvents that less readily lose a hydrogen atom.

Derivation of Kinetic Equations

The decomposition of cumene hydroperoxide thermally is not a simple first order reaction. When styrene is used as solvent an analysis of the steps in polymerization may reveal the cause of this. There are four stages; initiation, propagation, transfer, and termination. These may be expressed by the following equations.

1. Initiation

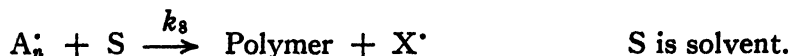
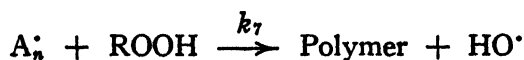
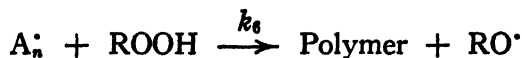


2. Propagation

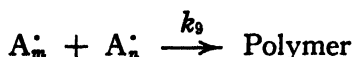


A_n^{\cdot} is a growing polymer radical of n monomer units.

3. Transfer



4. Termination



These equations assume that the values of k_5 , k_6 , k_7 , k_8 , and k_9 are independent of the nature of the end group and of the number of monomer units attached to the growing polymer radical. This assumption appears to be valid when the number of units is large. At a steady state, the rate of formation of any radical is equal to its rate of disappearance. Thus for the RO^{\cdot} radicals:

$$k_1(P) + k_6(P) \sum_{n=1}^{n=r} A_n^{\cdot} = k_2(RO^{\cdot})(M) \quad (P) = \text{conc. ROOH} \quad (1)$$

Similar equations may be formed in the HO^{\cdot} , X^{\cdot} , A_1^{\cdot} , A_2^{\cdot} , A_r^{\cdot} radicals as follows:

$$k_1(P) + k_7(P) \sum (A_n^{\cdot}) = k_3(HO^{\cdot})(M) \quad (2)$$

$$k_8(S) \sum (A_n^{\cdot}) = k_4(X^{\cdot})(M) \quad (3)$$

$$k_2(RO^{\cdot})(M) + k_3(HO^{\cdot})(M) + k_4(X^{\cdot})(M) = k_5(A_1^{\cdot})(M) + (k_6 + k_7)(A_1^{\cdot})(P) + k_8(A_1^{\cdot})(S) + k_9(A_1^{\cdot}) \sum (A_n^{\cdot}) \quad (4)$$

$$k_5(A_1^{\cdot})(M) = k_5(A_2^{\cdot})(M) + (k_6 + k_7)(A_2^{\cdot})(P) + k_8(A_2^{\cdot})(S) + k_9(A_2^{\cdot}) \sum (A_n^{\cdot}) \quad (5)$$

$$\text{-----}$$

$$\text{-----}$$

$$k_5(A_{r-1}^{\cdot})(M) = (k_6 + k_7)(A_r^{\cdot})(P) + k_8(A_r^{\cdot})(S) + k_9(A_r^{\cdot}) \sum (A_n^{\cdot}) \quad (r + 3)$$

Adding Equations (1) to $(r + 3)$

$$\sum A_n^{\cdot} = \left(\frac{2k_1(P)}{k_2} \right)^{\frac{1}{2}} \quad (1')$$

$$\text{But } \frac{-d(P)}{dt} = k_1(P) + (k_6 + k_7)(P) \sum (A_n^{\cdot}) \quad (2')$$

Substituting (1') in (2'):

$$\begin{aligned} \frac{-d(P)}{dt} &= k_1(P) + (k_6 + k_7) \left(\frac{2k_1(P)^3}{k_9} \right)^{\frac{1}{2}} \\ &= k_1(P) + K(P)^{3/2}, \text{ when } K = (k_6 + k_7) \left(\frac{2k_1}{k_9} \right)^{\frac{1}{2}} \quad (3') \end{aligned}$$

Thus assumption of Reactions 1 to 4 leads to a kinetic equation for the disappearance of cumene hydroperoxide involving the sum of a first and a three-halves order reaction. The deviation from first order is caused by the radical-induced decomposition or chain transfer step.

Integrating (3'):

$$\ln(1 + k/(P)^{\frac{1}{2}}) - \ln(1 + k/(P_0)^{\frac{1}{2}}) = \frac{k_1 t}{2}, \text{ where } k = k_1/K. \quad (4')$$

For two different values of P_0 , at any time t

$$\begin{aligned} \ln(1 + k/(P_1)^{\frac{1}{2}}) &= \ln(1 + k/(P_2)^{\frac{1}{2}}) + \ln C \\ 1/(P_1)^{\frac{1}{2}} &= C/(P_2)^{\frac{1}{2}} + (C - 1)/k. \end{aligned} \quad (5')$$

If these equations describe the polymerization accurately a plot of $1/(P_1)^{\frac{1}{2}}$ versus $1/(P_2)^{\frac{1}{2}}$ should give a straight line with slope C and intercept equal to $(C-1)/k$, from which a value k may be calculated. A plot of $\log(1 + k/(P)^{\frac{1}{2}})$ versus t should give a straight line with a slope of $k_1/2 \times 2.30$. If k_9 is known then $k_6 + k_7$ may be determined.

It should be noted that k_6 , the rate constant for propagation, does not appear in Equation (3'). Therefore Equations (3'), (4'), and (5') should hold for nonpolymerizing solvents that are reactive to RO^\cdot and OH^\cdot radicals if the same radical is produced by the reaction of RO^\cdot or OH^\cdot and the solvent. These equations are similar to those developed by Nozaki (19) for the decomposition of benzoyl peroxide in various solvents. The rate constants for transfer and termination would likely differ greatly from those obtained with styrene as solvent owing to the much shorter "chain" length and greater influence of terminal groups. The rate of decomposition in a polymerizing solvent is influenced by two factors. There is appreciable shrinkage during conversion of styrene to polystyrene; this causes a change in concentration of peroxide other than that due to the decomposition. In addition there is the question of whether polystyrene should be considered as solvent for the hydroperoxide or inert. The disappearance of hydroperoxide with an accompanying change in volume is not amenable to simple analyses, so further work was confined to mixed solvents in which both factors could be minimized.

Decomposition of Cumene Hydroperoxide in Mixed Solvents

The data collected, using styrene-benzene mixed solvent, are in Tables III and IV. The values of $1/(P_1)^{\frac{1}{2}}$ and $1/(P_2)^{\frac{1}{2}}$ are plotted in Fig. 5 while in Fig. 6 the values of $\log(1 + k/(P)^{\frac{1}{2}})$ are plotted against time. The curvature of Curves 5 and 6 of Fig. 6 is due possibly to depletion of the styrene in the dilute

TABLE III

DECOMPOSITION OF CUMENE HYDROPEROXIDE IN MIXED SOLVENTS

t , sec.	$(P_1)^*$, moles/l.	$(P_2)^*$, moles/l.	$1/(P_1)^{1/2}$	$1/(P_2)^{1/2}$	$1+k/(P_1)^{1/2}$	$1+k/(P_2)^{1/2}$
<i>Temperature 90.9° C. Styrene/benzene, 1 mole/4 moles</i>						
0.00 × 10 ⁴	9.96 × 10 ⁻³	4.70 × 10 ⁻⁴	10.02	4.61	2.645	1.755
0.24	9.90	4.64	10.05	4.64	2.650	1.760
0.48	9.82	4.60	10.09	4.66	2.655	1.765
0.72	9.78	4.54	10.11	4.69	2.660	1.770
0.96	9.74	4.47	10.13	4.73	2.660	1.775
1.44	9.67	4.39	10.16	4.77	2.665	1.780
1.92	9.62	4.29	10.19	4.83	2.670	1.790
2.40	9.49	4.23	10.26	4.86	2.680	1.795
3.96	8.73	3.89	10.70	5.07	2.755	1.830
5.40	8.62	3.68	10.76	5.21	2.765	1.855
8.64	8.06	3.45	11.13	5.38	2.825	1.885
<i>Temperature 109.8° C. Styrene/benzene, 1 mole/4 moles</i>						
0.00 × 10 ³	9.22 × 10 ⁻³	4.53 × 10 ⁻³	10.41	4.70	4.34	2.505
1.80	8.94	4.35	10.58	4.79	4.38	2.535
3.60	8.78	4.16	10.67	4.90	4.42	2.570
5.40	8.50	4.06	10.85	4.96	4.48	2.585
7.20	8.30	3.92	10.98	5.05	4.52	2.615
9.00	7.87	3.75	11.27	5.16	4.60	2.660
10.80	7.63	3.69	11.45	5.20	4.66	2.665
12.60	7.49	3.57	11.55	5.29	4.70	2.695
14.40	7.41	3.44	11.61	5.39	4.72	2.725
16.20	7.25	3.38	11.75	5.44	4.76	2.740
18.00	7.09	3.31	11.88	5.50	4.80	2.760
<i>Temperature 90.0° C. Styrene/benzene, 1 mole/9 moles</i>						
0.00 × 10 ⁴	9.64 × 10 ⁻³	4.56 × 10 ⁻²	10.19	4.68	6.51	3.54
1.10	9.37	4.41	10.33	4.76	6.60	3.58
2.15	9.12	4.30	10.48	4.83	6.68	3.62
6.50	8.25	3.86	11.01	5.09	6.97	3.76
8.65	7.99	3.69	11.20	5.21	7.07	3.82
15.10	7.27	3.39	11.73	5.44	7.36	3.95
17.30	7.15	3.29	11.82	5.52	7.41	3.99
25.90	6.70	2.99	12.21	5.79	7.63	4.14
28.10	6.60	2.94	12.30	5.94	7.66	4.22

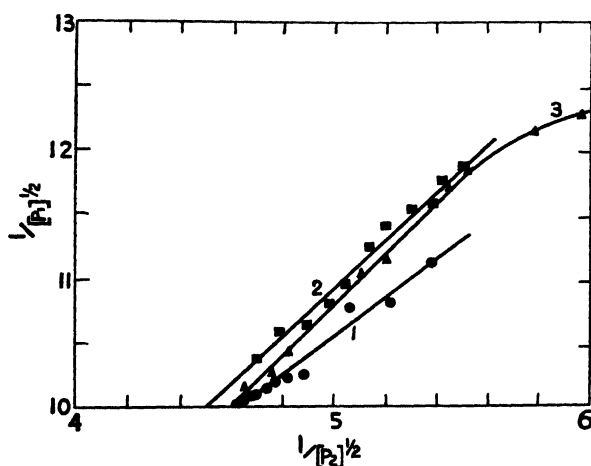
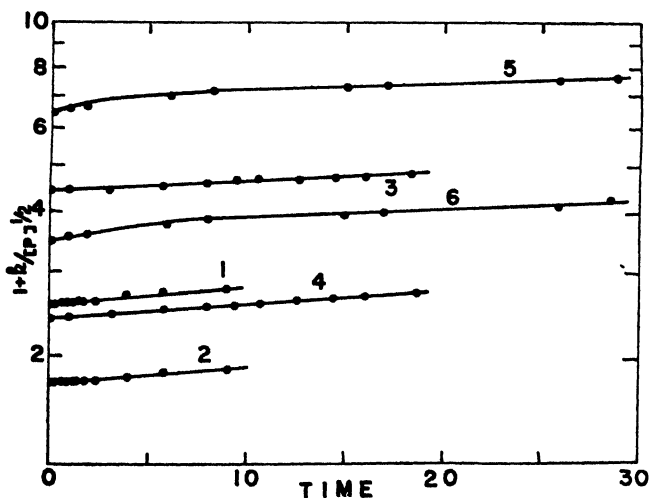
* These values were calculated using the actual volume of the solution at the time of sampling.

solution used. The extrapolations in Fig. 5 are uncertain and the decomposition could not be followed further owing to formation of polystyrene with resulting shrinkage of the volume, increase in viscosity, and decrease in the styrene-to-benzene ratio.

From the data in Table IV the value of the rate constant for the unimolecular decomposition of cumene hydroperoxide into RO^\cdot and OH^\cdot radicals was calculated and found to be $2.7 \times 10^{12} e^{-30,400/RT} \text{ sec.}^{-1}$ between 90.9° and

TABLE IV
 RATE CONSTANTS IN MIXED SOLVENTS

Temperature, °C.	(P ₀) moles/l.	k ₁	k ₀ + k ₁ , (moles/l) ⁻¹ sec. ⁻¹ *
90.9	9.96 × 10 ⁻³	1.50 × 10 ⁻⁶ sec. ⁻¹	13.5
90.9	4.70 × 10 ⁻³	1.50 × 10 ⁻⁶	13.5
109.8	9.22 × 10 ⁻³	1.20 × 10 ⁻⁶	21.0
109.8	4.53 × 10 ⁻³	1.20 × 10 ⁻⁶	21.0


 FIG. 5. Plot of $1/P^{1/2}$ at constant times for two initial values of cumene hydroperoxide concentration P . Curve 1. At 90.9° C. in styrene-benzene, molar ratio 1 : 4. Curve 2. Same at 109.8° C. Curve 3. At 90.0° C. in styrene-benzene, molar ratio 1 : 9.

 FIG. 6. Plot of $\log(1 + k/P^{1/2})$ versus time. Curve 1; 9.96 × 10⁻³ molar solution of cumene hydroperoxide (concentration P) in styrene-benzene, molar ratio 1 : 4, at 90.9° C. Curve 2; 4.70 × 10⁻³ molar solution in same. Curve 3; 9.22 × 10⁻³ molar solution in same at 109.8° C. Curve 4; 4.53 × 10⁻³ molar solution in same. Curve 5; 9.64 × 10⁻³ molar solution in styrene-benzene, molar ratio 1 : 9, at 90.0° C. Curve 6; 4.56 × 10⁻³ molar solution in same. Curves 1, 2, 5, and 6; time is seconds × 10⁻⁴; Curves 3 and 4; seconds × 10⁻³.

109.8° C. The value of the energy of activation (30.4 kcal. per mole) is higher than the previous estimate because the latter included the effect of the radical-induced decomposition.

Assuming (2) a termination rate constant

$$k_9 = 3.07 \times 10^8 \times e^{-2800/RT} \text{ (mole/l.) sec.}^{-1}$$

the value of $k_6 + k_7$ is $1.00 \times 10^8 e^{-6500/RT} \text{ (mole/l.)}^{-1} \text{ sec.}^{-1}$.

Attempts to gain accuracy by following the reaction further must also take into account changes in the concentration of styrene in benzene. That this is appreciable is shown in comparing the initial rate of decomposition of cumene hydroperoxide in Table III. When the more dilute solution of styrene is used the initial rate, expressed as a percentage of the original concentration per unit of time, is very nearly independent of the concentration, in contrast with the results using the solvent richer in styrene, where the rate is faster when the initial hydroperoxide concentration is greater.

This effect is accentuated when pure benzene is used as a solvent. The results are in Table V.

TABLE V
DECOMPOSITION OF CUMENE HYDROPEROXIDE IN BENZENE AT 90.9° C.

Time, hr.	% unreacted cumene hydroperoxide	
	2.210×10^{-2} molar solution	1.102×10^{-1} molar solution
0.0	100	100
96	83.8	92.6
168	34.4	81.7

The results indicate the autocatalytic effect of increase in rate of decomposition with time but in addition show a relatively more rapid rate of decomposition in dilute solution than in concentrated solution. The cause of this was not elucidated. This effect might be related to some of the results obtained during emulsion copolymerization using this hydroperoxide. It was decided, however, to defer any further consideration and to include it in the study of the catalyzed decomposition of cumene hydroperoxide, which will be a separate report.

Analysis of the Products of Decomposition in Cumene

To obtain information on the reactions of the radicals formed from cumene hydroperoxide an attempt was made to analyze the products formed in cumene at 90.5° C. Cumene was chosen as the solvent rather than styrene because of the difficulty of identifying the hydroperoxide fragments in the larger polystyrene molecule.

Numerous preliminary experiments were considered unsuitable because of the rapid temperature increase during the autocatalytic stage. This was

overcome by increment addition of the hydroperoxide. The reaction products were prepared on a macro scale by reacting 0.2 mole of cumene hydroperoxide in 1.8 mole of cumene. Distilled cumene, 1.6 moles, was added to a 500 ml. round-bottomed flask provided with a thermometer well and fitted with a 100 ml. graduated addition flask, the take-off tube of which was connected to a trap immersed in a dry ice - ethanol bath and a gas measuring set. The flask was placed in a dry ice - ethanol bath and subjected to the same treatment as the solutions in the rate studies with regard to evacuation and nitrogen flushing, except that an additional nitrogen flushing was included and the cumene was left under a pressure of $2\frac{1}{2}$ p.s.i. of nitrogen. The flask was placed in a constant temperature bath at 90.5°C . and after equilibrium was obtained was vented to the atmosphere. A solution containing 0.2 mole of distilled cumene and 0.2 mole of the hydroperoxide was added to the addition flask, and the top was closed with a glass stopper. Enough of the solution was added to give an initial hydroperoxide concentration of 2%. After about two hours a slight increase in temperature was noticed. The solution was added in increments over a five-hour period so that the temperature of the reaction mixture was held at $90.5 \pm 1.0^{\circ}\text{C}$. The reaction was allowed to continue for two hours after all the cumene hydroperoxide solution had been added.

The products were then subjected to analysis. The volume of liberated gas was found to be very small and probably could be accounted for fully by the increased vapor pressure of the reaction mixture caused by the presence of volatile products. No liquid was condensed in the trap; this demonstrated that the formation of very volatile products does not occur. The liquid in the flask consisted of two layers—a very small lower watery layer (2 ml.) and a much larger upper oily layer. Determination of the residual peroxide in the upper layer revealed that less than 0.1% of the initial weight of CHP remained. The upper layer was also analyzed for acetophenone (1.90 gm. or 0.016 mole) and phenol (1.70 gm. or 0.018 mole), using an ultraviolet absorption method. These values were corrected for the absorption caused by the cumene, which is probably the principal interfering compound at the wave lengths used (241 $m\mu$ for acetophenone and 273 $m\mu$ for phenol). Both layers were then distilled under 3 mm. of pressure in a 15 in. unpacked column until the vapor temperature reached 40°C . This distillate was fractionated at atmospheric pressure in a 100 plate Podbielniak column at a 30 : 1 reflux ratio, using stripped diethylbenzene chaser, which boiled at 178°C . From this distillation were recovered the products shown in Table VI.

The residue from the vacuum distillation was distilled at 2 mm. pressure until the vapor temperature reached 60°C . This distillate was extracted twice with 10 ml. portions of water at 70°C . to remove the phenol. The water was removed from the extract under vacuum at room temperature. Phenol, 1.40 gm. (0.015 mole), which melted at 40°C ., was recovered. The non-extracted portion probably contained acetophenone and α,α' -dimethylbenzyl alcohol, the weight of which was calculated by difference (4.80 gm. or 0.035 mole). The ratio of alcohol to acetophenone agrees approximately with the

TABLE VI
ANALYSIS OF DECOMPOSITION PRODUCTS

Product	Weight		B.p. at 760 mm.	η_{sp}^{25}
	Gm.	Moles		
Acetone	7.55	0.130	56.2	1.3571
Water	1.55	0.087	100.0	—
Cumene	206.2	0.715	152.2	1.4889
Higher boiling compounds	15.00	—	—	—

ratio given for these impurities in a typical sample of commercial cumene hydroperoxide where they are formed by its decomposition during manufacture. This agreement tends to support the validity of the value given here for the alcohol. A summary of the weights of all the products identified is presented in Table VII.

TABLE VII
ANALYSIS OF PRODUCTS OF DECOMPOSITION

Product	No. of moles per mole hydroperoxide
Acetone	0.65
Acetophenone	0.08
Phenol	0.09
Water	0.43
α, α' -Dimethylbenzyl alcohol (calculated)	0.17
Cumene (reacted)	0.42

These are not all the products in the reaction mixture but they are the only ones that have been identified. However it is not very likely that the side reactions that take place in cumene are important from the standpoint of polymerization initiation. No acetone was isolated from the decomposition of 0.2 mole of cumene hydroperoxide in 1.8 moles of styrene at 90.5° C. It is not feasible to analyze for acetophenone in styrene because of its strong absorption at the wave length used. However, in view of the work done on the macro decomposition in cumene, no formation of acetophenone would be expected. It seems that the $C_6H_5C(CH_3)_2O\cdot$ radicals are able to initiate polymerization before they can break down to acetone and a phenyl radical.

Effect of Shortstops

It was thought that some concept of the mechanism by which a shortstop brings a halt to the polymerization reaction could be elucidated by a study of the effect of shortstops on the thermal decomposition of cumene hydroperoxide in styrene. Subsequently results were obtained *in vacuo* for the two

shortstops used currently in the low temperature recipes, 2,5-ditertiarybutylhydroquinone and 2,4-dinitrochlorobenzene, and other related compounds known to be effective (11). An initial cumene hydroperoxide concentration of 0.2 mole per kgm. of final solution was chosen and 0.02 mole per kgm. of solution of a shortstop or related compound was added to the hydroperoxide solution in styrene, previously cooled to a temperature just above its freezing point and kept at this temperature or lower until the reaction tubes were immersed in the bath at 90.6° C. In addition to the results given in Table VIII an attempt was made to study the effect of hydroquinone, which

TABLE VIII
UNREACTED CUMENE HYDROPEROXIDE, % OF INITIAL WEIGHT

Reaction time, min.	No shortstop	2,5-Ditertiary-butylhydroquinone		2,4-Dinitrochlorobenzene	2,6-Ditertiary-butyl-4-methylphenol	Phenyl- β -naphthylamine
0.00*	100.0	90.0†	90.0‡	100.0	99.5	97.5
20.00	88.3	88.4		94.0	85.1	93.3
40.00	77.8	85.4		90.0	88.9	88.1
60.00	67.0	81.5	83.2	80.0	82.6	82.6
80.00	51.9	79.0		80.9	78.4	76.1
100.00	34.0	76.2		79.2	68.2	68.3
120.00	16.4	73.5	74.0	78.0	58.7	61.2
140.00	3.8	70.5		74.1	48.2	52.6
160.00	—	66.8		71.2	42.6	37.1
180.00	—	65.1	59.5	68.3	38.8	32.7
200.00	—	62.9		65.1	34.0	32.7
220.00	—	58.6		62.0	29.0	— §
240.00	—	46.0	45.4	44.1	— §	— §

† Eastman Kodak Technical.

‡ Monsanto recrystallized.

§ Too viscous to analyze.

* Samples removed from solution at -10° C.

is the shortstop used to stop persulphate-initiated polymerization, and *p*-benzylaminophenol and *p*-nitrobenzeneazo-3,4,5-trihydroxyphenol, photographic develops that were found to stop the reaction satisfactorily in the polymerization laboratory (11). These attempts were unsuccessful because of the insolubility of hydroquinone in the solution and the interfering color of the latter two compounds and/or their derivatives which completely masks the end point of the titration in the method of analysis used.

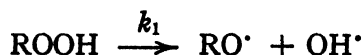
From these results it would seem that 2,5-ditertiarybutylhydroquinone reacts with equimolar amounts of cumene hydroperoxide in a styrene solution at -10° C. The resulting products are powerful retarders for the decomposition of the hydroperoxide in styrene at elevated temperatures. 2,4-Dinitrochlorobenzene, 2,6-ditertiarybutyl-4-methyl phenol and phenyl- β -naphthylamine do not react under these conditions mentioned but they do retard the decomposition in styrene at elevated temperatures. 2,4-Dinitrochlorobenzene is a more powerful retarder than is either of the other two.

Discussion

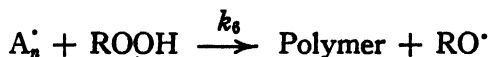
Cumene hydroperoxide would appear to enter into two phases of polymerization. The first is the formation of free radicals either by unimolecular dissociation, or by reaction with solvents or activators, or by chain transfer with solvents or a growing polymer radical. These free radicals in turn react with a monomer to start a growing polymer chain. The second phase is the stopping of the polymerization reaction by terminating the growing polymer chains and destroying the residual initiator or otherwise rendering it inactive.

The thermal decomposition of cumene hydroperoxide in a solution of monomer such as styrene is the sum of a first order and a three-halves order reaction. The first order reaction arises from the unimolecular decomposition. The three-halves order reaction arises from the radical-induced chain transfer reaction. In pure styrene the reaction rapidly becomes autocatalytic.

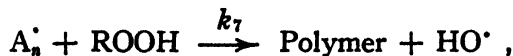
The relative amounts of peroxide consumed in the two reactions is of interest since the ratio of the two types of decomposition enters into the molecular weight distribution studies of the resulting polymers. If Reaction (I) is



and Reaction (II) is the sum of



and



then $\left. \frac{-d(P)}{dt} \right|_{(I)} = k_1 (P)$ (rate of disappearance of hydroperoxide by Reaction (I))

$$\begin{aligned} \left. \frac{-d(P)}{dt} \right|_{(II)} &= (k_6 + k_7) (P) \Sigma (A_n^\cdot) \text{ (disappearance by Reaction (II))} \\ &= (k_6 + k_7) \left(\frac{2k_1}{k_9} \right)^{\frac{1}{2}} (P)^{3/2} \\ &= K (P)^{3/2}. \end{aligned}$$

$$\text{Therefore } \frac{-d(P)|_{(I)}}{-d(P)|_{(II)}} = \frac{k_1}{K} \cdot \frac{1}{(P)^{\frac{1}{2}}} \text{ or } \frac{-\Delta(P)|_{(I)}}{-\Delta(P)|_{(II)}} = \frac{k}{(P)^{\frac{1}{2}}}$$

$$\text{or } \frac{\Delta(P)|_{(II)}}{\Delta(P)|_{(I)}} = P^{\frac{1}{2}}/k.$$

From this analysis it can be seen that the relative amount of cumene hydroperoxide consumed by transfer should increase with increasing concentration and decreasing temperature since k decreases with decreasing temperature.

However, not all of the radicals need start polymerization. None do in the absence of monomers. Following the initial split of the cumene hydroperoxide into $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O}^\cdot$ radicals and OH^\cdot radicals, a chain of events may occur.

Under the conditions of the experiments in cumene most of the $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2\text{O}^\cdot$ radicals lose a radical and form a ketone; the tendency is for the radical to lose the phenyl radical and form acetone in preference to losing a methyl radical and forming acetophenone. Kharasch (12) suggests that the mechanism of these steps is different.

The OH^\cdot radicals are not accounted for as completely. Probably some abstract a hydrogen atom from cumene to form water. The cumene disappears in about the same molar proportions as the water formed. Others react with free phenyl radicals to yield phenol. Possibly the α,α' -dimethylbenzyl alcohol may be accounted for by the recombination of the $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2^\cdot$ and OH^\cdot radicals. Its formation from the $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2\text{O}^\cdot$ radical by the abstraction of a hydrogen atom from cumene does not seem to be as probable. Other unidentified products remained and may account for the residual portion of the material balance. The products appeared to be higher hydrocarbons, possibly with hydroxyl groups.

The stopping of polymerization appears to occur by two distinct mechanisms. 2,5-Ditertiarybutylhydroquinone and 2,4-dinitrochlorobenzene, which are each considered good stopping agents, exemplify the two types. The former reacts quantitatively and rapidly with the cumene hydroperoxide at -10°C . thereby destroying the initiator system. Presumably the hydroquinone is converted to an inactive semiquinone or quinone. The 2,4-dinitrochlorobenzene on the other hand acts as a polymerization retarder by effectively inhibiting the decomposition of cumene hydroperoxide. While the mechanism of this action is not clear it may be related to systems described by Bovey and Kolthoff (4) in which free radicals are consumed and normal propagation is thereby eliminated. In the same category but less effective as inhibitors are the other soluble shortstops studied. Lack of oil solubility is, of course, a limitation that excludes such familiar stopping agents as hydroquinone and sodium sulphide.

The desirable shortstop would seem to be one that was sufficiently oil soluble to enter the emulsion droplet and react with the residual initiator and yet be sufficiently soluble in the aqueous phase to diffuse rapidly from the source of stopping agent to the emulsion droplet.

The thermal decomposition of cumene hydroperoxide requires such elevated temperatures that it has no role in low temperature polymerization reactions at or below 5°C . Catalytic and induced decomposition must account for all of the initiation of polymerization obtained. Likewise in the absence of a catalyst little effect would be expected from any residual initiator left in the polymer while the latter was being coagulated and dried for short periods at 70° to 80°C . The effect might become noticeable during longer drying periods or during the short periods at much higher temperatures (150°C .) as encountered during the degradation of the polymer during compounding and curing. In view of these findings only the catalytic decomposition will receive further study.

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THE EFFECT OF CHAIN LENGTH ON THE INTRINSIC VISCOSITY - TEMPERATURE COEFFICIENT OF LINEAR HIGH POLYMERS¹

BY L. H. CRAGG AND J. E. SIMKINS²

Abstract

Careful measurements of the intrinsic viscosities of three fractions of polystyrene, ranging in molecular weight from 160,000 to 1,350,000, have been made over a 40° C. range of temperature in a good solvent (toluene) and a poor one (toluene - 30% 1-butanol). These, together with similar but somewhat less accurate measurements with five fractions of GR-S, show clearly that solvent effects on the intrinsic viscosity are strongly dependent on molecular weight for linear flexible polymers, and give additional support to the concept that the differences in the intrinsic viscosity of such a polymer in good or poor solvents are due primarily to differences in the looseness or tightness of coiling of its flexible molecules in solution.

Although the viscosity of a dilute solution of a high polymeric substance is the viscosity of the solvent modified by the presence of the solute, the extent of the modification is out of all proportion to the number of solute molecules present. The disproportionate effect of these molecules may be attributed to their unusual size; for linear macromolecules of a given homologous polymeric series the effect is greater the longer the molecules are, that is, the higher their molecular weight. This effect of the solute molecules is isolated when the specific viscosity, $\eta_r - 1$, or better the reduced viscosity, $\frac{\eta_r - 1}{c}$, is calculated, and the secondary effect of solute molecules on each other is eliminated in the intrinsic viscosity, $[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta_r - 1}{c}$. Thus the intrinsic viscosity should be a function of chain length. For many linear polymers the relation is given by the empirical equation $[\eta] = KM^a$, where M is the molecular weight of the polymer if all its molecules are identical or its "viscosity-average molecular weight" if they are not, and K and a are empirical constants (7). Unfortunately, even with a given polymer, K and a must be evaluated for each different solvent, for the intrinsic viscosity (unlike the limiting value of the reduced osmotic pressure, $\left(\frac{\pi}{c}\right)$) varies from solvent to solvent. This effect must be due to solvent-solute interaction of some kind. It was at one time attributed to solvation of the polymer molecules and to the change in their effective size and shape resulting from the addition of a solvation sheath. More recently the belief has grown that, although this effect of solvation may make its contribution (and undoubtedly does in many

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systems (6, 23)), the effect of solvent on flexible polymer molecules is largely due to its influence on the shape that the polymer molecules themselves assume in solution (3, 15, 17, 21).

A flexible linear polymer molecule may be thought of as a chain of segments jointed together by more or less flexible links. In an "energetically favorable" (3) solvent, segments are attracted more by the surrounding solvent than they are by other segments in the chain, and as a result the flexible molecule tends to be stretched out. Such a solvent we shall term "good." By contrast, in an energetically unfavorable (or "poor") solvent the forces between segments are dominant and the polymer molecule draws in upon itself, assuming a randomly coiled configuration; the poorer the solvent the more tightly coiled is the molecule. Thus the intrinsic viscosity is greater in the good solvent.

Of course by "shape" (or "configuration") is meant the average shape, for the molecules in consequence of their flexibility are undergoing what has been called "internal Brownian movement" and are changing shape, and hence the degree of coiling, continuously and rapidly. The most probable shape lies between the elongated one in a good solvent and the tightly coiled one in a poor solvent. Raising the temperature and therefore the vigor of this internal Brownian movement would favor the more probable configuration, and hence decrease the intrinsic viscosity of a polymer in a good solvent and increase it in a poor solvent. By adding a nonsolvent to a solvent it should be possible to change gradually from a good solvent to a poor solvent and therefore to change from a high to a low intrinsic viscosity and from a negative to a positive slope of the intrinsic viscosity vs. temperature curve.

These and other predictions have stood the test of experiment (2, 3, 4, 10). In a paper describing some of the experimental vindications (10) another consequence of the theory was suggested, namely, that "one would expect that much greater effects would be observed with very long molecules than with short ones" (or, in other words, the changes in intrinsic viscosity and the slope that were mentioned above should be more marked with the larger molecules). Subsequently, fractionated samples of GR-S and of polystyrene, varying sufficiently in molecular weight, became available, and the expectation could be tested.

Experimental

1. MATERIALS

Solvents and Nonsolvents

Benzene — (Steel Company of Canada), ASTM Industrial Grade, redistilled and dried over sodium; b.p. 80.5° C.

Toluene— (Steel Company of Canada), "nitration grade," redistilled; b.p. 110° C.

Methanol — (Carbide and Carbon Chemical Company), dried over calcium oxide and redistilled; b.p. 63.7° C.

1-Butanol— (Eastman Kodak), Reagent Grade.

Polymers

GR-S

The unfractionated material was a normal plant sample obtained in bale form from Polymer Corporation, Limited, Sarnia, on July 9, 1946. It has been described elsewhere (10); no change in intrinsic viscosity was observed with time. Its viscosity-average molecular weight* was 224,000.

Five fractions of molecular weight (\bar{M}_v)* 631,000, 561,000, 274,000, 124,000, and 21,500, respectively, were obtained from D. F. Switzer (24, 25). They were numbers 1, 2, 7, 10, and 14 of the 14 fractions obtained by him in a primary fractionation by precipitation from 2% solution in benzene, using methanol as precipitant. They were obtained as solutions (approximately 0.5% in polymer) in benzene containing a small proportion of methanol (always less than 1.8%). Subsequent work by Switzer has proved that the presence of these small amounts of methanol does not affect the values of intrinsic viscosity by more than the experimental error, $\pm 2\%$.

Polystyrene

A sample of unfractionated polymer and of three fractions from it were obtained from Monsanto Chemical Company. These materials were prepared as follows:

"Commercial monostyrene containing about 10 ppm. of *paratertiary butyl catechol* was polymerized in bulk at 93° C. without the use of catalyst. After 12 hours, 15% conversion was reached and the reaction was stopped by cooling to 20° C. in less than 15 minutes. 0.1% hydroquinone was then added. The polymer was isolated by dripping the solution of polymer in monomer into 10 volumes of methanol; it was filtered and washed with methanol again. The polymer was then dissolved in methyl ethyl ketone (MEK) to make a 2% solution and then precipitated in the form of a porous thread having a high surface/weight ratio by running a fine stream of the polymer solution into 10 volumes of stirred methanol.

"The twice precipitated material was then dissolved in methyl ethyl ketone to make a 1.5% solution; methanol was added until the solution became cloudy. The temperature was raised until all the material was again dissolved, then lowered slowly to precipitate a fraction as a gel. This gel was drawn off, dissolved in MEK and again precipitated with a high surface/weight ratio in ethanol.

"Altogether, 40 fractions were obtained. The fractions were vacuum dried at room temperature and stored at room temperature under CO₂ in the absence of light."

The samples used in this study are of fractions 3, 21, 35, and of the original polymer. The molecular weights, determined from intrinsic viscosities

* Calculated from the values of $[\eta]$ at 25° C., using the equation of Scott, Carter, and Magat (20).

calibrated by light scattering measurements, were given as 1,350,000, 525,000, 160,000, and 730,000 respectively (the last a viscosity-average).

2. APPARATUS

The viscometers used were of the Ostwald-Cannon-Fenske type (ASTM 50); they had been carefully calibrated over the whole range of flow times encountered. The various temperatures of measurement were maintained in constant-temperature baths regulated to $\pm 0.02^\circ \text{C}$. Specially designed viscometer clamps incorporating standard-taper pins made it possible to transfer a viscometer from bath to bath conveniently and yet be sure that the mounting in each bath was reproducibly vertical. After each such transfer the viscometer and contents were allowed to equilibrate for 10 min. before flow times were measured.

3. INTRINSIC VISCOSITY DETERMINATIONS

Flow times were measured as before (10) in duplicate or triplicate (or until agreement to ± 0.1 sec. was obtained), first at the lowest temperature and then at successively higher temperatures. Even in the polystyrene experiments, which involved successive measurements at five temperatures, there was neither significant evaporation nor degradation, as proved by the observation that the flow times measured at 25°C . after such a run were exactly the same as at its beginning. Concentrations of the solutions were calculated as weight per cent (grams solute per 100 gm. solution) and corrected to the usual units (grams per 100 ml.) at each temperature by multiplying by the density of the solution at that temperature. (Actually the density of the solvent was used but the error introduced by this approximation is negligible. The densities of the pure solvents at the various temperatures were taken from the literature (18); those for the mixed solvents were measured.)

With polystyrene solutions, the *concentration* was calculated from the measured weights of dry polymer and solvent used in preparing the solution.

With GR-S, the concentration could not be determined in this way because the fractions used were available only as solutions (from which they could not be separated by evaporation because of gel formation); it was therefore determined by evaporating a weighed amount of solution to constant weight at 70°C . This method is more precise than accurate but since we are concerned with relative values precision is more important than accuracy.

Intrinsic viscosities were determined from values of flow time and concentration, as follows:

(a) GR-S

Solutions in benzene were prepared of four concentrations from 0.05 to 0.4 gm. per 100 ml., values of the inherent flow time (9) $\frac{\ln t_r}{c}$ calculated, and the intrinsic flow time $[\eta]$ determined by extrapolation. Although kinetic

energy corrections were not applied, the viscometers had been calibrated and it was known that the intrinsic viscosity $[\eta]$ would differ from $[\iota]$ by not more than 3 or 4%.

Solutions in mixed solvent (benzene – 13.2% methanol) were prepared of only one concentration and the intrinsic viscosity calculated by the equation

$$[\iota] = \frac{8 (\iota_r - 1)}{c} \quad (11)$$

This one-point method is known to be somewhat less accurate for the highest fractions of GR-S than for intermediate and low fractions or for unfractionated material (24, 25) but the error introduced in $[\eta]$ is still small.

(b) Polystyrene

All values of $[\eta]$ were obtained by extrapolation, using the values of inherent kinematic viscosity $\frac{\ln \nu_r}{c}$ (9) for three or four solutions ranging in concentration from 0.1 to 0.4 gm. per 100 ml.; the values of $\frac{\ln \nu_r}{c}$ were calculated from flow times by applying the kinetic energy correction. Because of these two refinements, and because with polystyrene the values of the concentration, c , were more accurate, the values of $[\eta]$ in the polystyrene study are more accurate than in the corresponding GR-S study.

Results

For GR-S, benzene is neither a very good nor a very poor solvent, for the $[\eta]$ vs. θ (temperature) curves are practically horizontal (10, 19). It can be made a poor solvent by the addition of a nonsolvent; at 18.3 vol. % methanol, precipitation begins at 15° C. for original polymer. Accordingly benzene-methanol containing 15 vol. % (13.2 wt. %) methanol was selected as a solvent that would be poor without being too poor. Intrinsic viscosities of the various fractions of GR-S and of the unfractionated material, as measured in this solvent at three temperatures, 15°, 35°, and 50° (or 55°) C., are shown graphically in Fig. 1. For comparison the variation of $[\eta]$ with temperature in pure benzene and in the mixed solvent is shown, for a high and a low fraction, in Fig. 2. (For lack of sufficient material, measurements in pure benzene could not be made with all fractions of GR-S. Thus with F-1 the intrinsic viscosity at 25° C. is that determined by Switzer (24, 25) and the curve is drawn in accordance with the general experience in this laboratory that the $[\eta]$ vs. θ line for GR-S and for GR-S fractions in benzene is always practically horizontal.) For polystyrene, toluene is a good solvent, giving a negative value of $\frac{d[\eta]}{d\theta}$, and toluene – 1-butanol containing 30% (by weight) of 1-butanol is a poor solvent (at 25° C. precipitation begins at *ca.* 38% butanol). The experimental data for the polystyrene-toluene and polystyrene-toluene-butanol systems at 25°, 35°, 45°, 55°, and 65° C. are given in Tables I and II and in Figs. 3 and 4. There is a definite suggestion that with the poor solvent the points lie on a curve slightly convex upwards, but the

evidence for the curvature is not sufficiently conclusive to offset the appeal of the straight line. (It should be noted, however, that working with polyisobutylene fractions in a poor solvent over a larger range of temperature — 0°

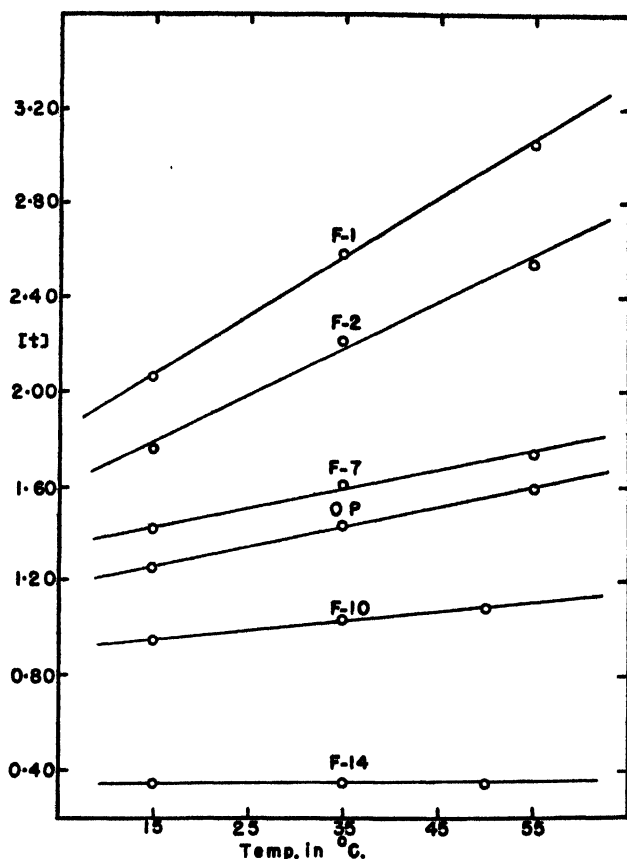


FIG. 1. Variation of intrinsic viscosity with temperature for GR-S (five fractions and the original polymer, OP) in benzene-methanol. The molecular weights (\bar{M}_v) are: OP 244,000, F-1 631,000, F-2 561,000, F-7 274,000, F-10 124,000, and F-14 21,500.

to 90° C. — Fox and Flory (16) have found experimental and theoretical evidence for a downward curvature.)

Discussion

The behavior of both GR-S and polystyrene, as indicated in these results, is just what was predicted. For example, the marked increase, with increasing molecular weight, of the slope $d[\eta]/d\theta$ in poor solvent that is evident in Figs. 1 to 4 is easily accounted for on the basis of uncoiling molecules: if an increase in temperature tends to uncoil the molecules in a poor solvent then even with the same degree of uncoiling the increase in linear dimension should be greater with the longer molecules.

Actually however one would expect the degree of uncoiling to be not the same but greater with the longer molecules. The flexibility of chain molecules

is by no means unlimited. Even the most flexible ones must do their bending gradually (like garden hose) and this puts a limit on the tightness of coiling that is possible. Furthermore this flexibility — or lack of it — is inherent in

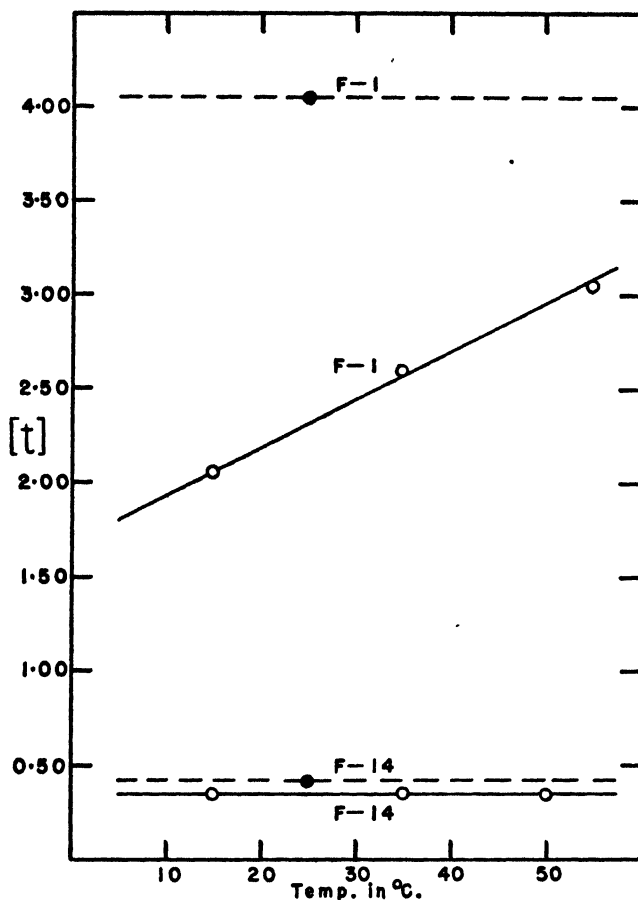


FIG. 2. Comparison of intrinsic viscosity - temperature behavior of high and low fractions of GR-S in good and poor solvents.

— ● — ● — in benzene.
— ○ — ○ — in benzene-methanol.

the structure of the chain and independent of its length. More precisely, the *intensive* flexibility (f. per unit length) of a long molecule is the same as that of a short molecule even though its *extensive* flexibility (f. for the molecule as a whole) is much greater. Accordingly, the ratio of the length of the molecule when extended to its length when coiled up should be greater for long molecules, and any effect resulting from uncoiling, whether as a consequence of an increase in temperature or of a change from poor to good solvent, should be *relatively* greater for the long molecules. In terms of our data, then, both the ratio $[\eta]_{\text{good}}/[\eta]_{\text{poor}}$ at any given temperature, and the relative slope $d[\eta]/d\theta \cdot [\eta]$ at

TABLE I

VARIATION OF INTRINSIC VISCOSITY WITH TEMPERATURE: POLYSTYRENE IN TOLUENE

Sample	\bar{M}_v	Intrinsic viscosity*				
		25° C.	35° C.	45° C.	55° C.	65° C.
F-3	1,350,000	2.30	2.29	2.28	2.29	2.28
F-21	525,000	1.32	1.31 ₆	1.32	1.32	1.30
F-35	160,000	0.57	0.57	0.57	0.56	0.57
Unfractd.	730,000	1.62	1.62	1.60	1.59	1.60

* Because of the great advantage in routine measurement of a one-point method for determining intrinsic viscosity, it is important to note that values of $[\eta]$ calculated from measurements of t_r at only one concentration, $c = 0.20 \pm 0.01$ gm. per 100 ml. solution, using the modified Baker equation (11)

$$[\eta] = \frac{n (t_r^n - 1)}{c}$$

with a value of $n = 3$, differed from those recorded in the table by an amount that was in only one instance more, and was usually less, than the experimental error, ± 0.02 , of the extrapolated value.

TABLE II

VARIATION OF INTRINSIC VISCOSITY WITH TEMPERATURE: POLYSTYRENE IN TOLUENE-1-BUTANOL (30%)

Sample	\bar{M}_v	Intrinsic viscosity				
		25° C.	35° C.	45° C.	55° C.	65° C.
F-3	1,350,000	1.22	1.34	1.43	1.52	1.60
F-21	525,000	0.77	0.82	0.87	0.91	0.94
F-35	160,000	0.39	0.40	0.42	0.43	0.43
Unfractd.	730,000	0.90	0.98	1.04	1.11	1.14

TABLE III

COMPARISON OF THE BEHAVIOR OF HIGH, INTERMEDIATE, AND LOW FRACTIONS OF POLYSTYRENE

	F-3	F-21	F-35
\bar{M}_v	1,350,000	525,000	169,000
$[\eta]_{\text{good}}/[\eta]_{\text{poor}}$ at 25° C.	1.89	1.71	1.46
$d[\eta]/d\theta \cdot [\eta]_{25}$ in poor solvent*	0.0078	0.0058	0.0026

* These values are calculated from the straight lines drawn through the points of Fig. 3. The same trend would be observed if curved lines had been drawn and slopes determined at 25° C.

any temperature, should be greater for the high fractions than for the low ones. Values of these functions at 25° C. calculated from the data for polystyrene are given in Table III. These, too, are in accord with expectations.

Such excellent agreement with predictions does not, of course, establish the validity of the theory that the solvent affects the shape of the polymer molecule dissolved in it, but it certainly does add support to it. Other strong evidence

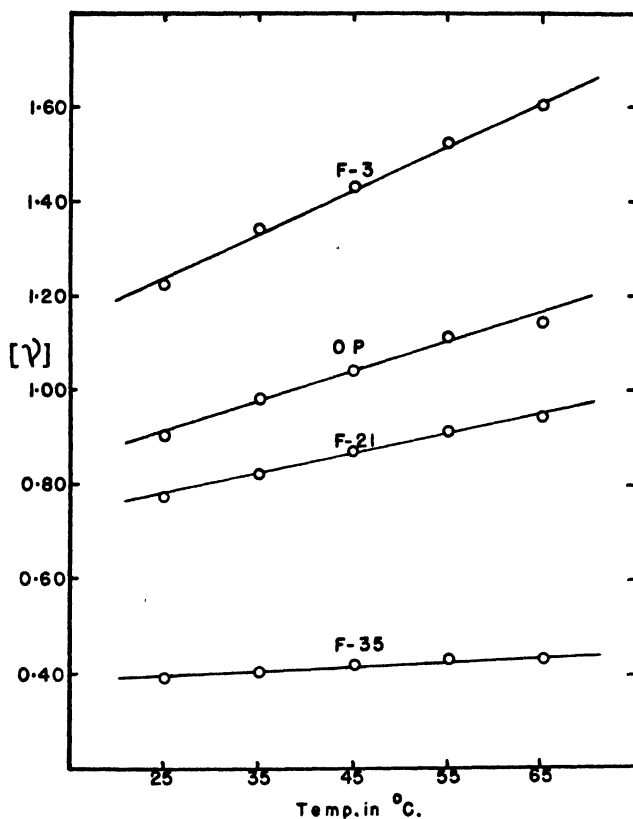


FIG. 3. Variation of intrinsic viscosity with temperature for polystyrene (three fractions and the original polymer) in toluene-butanol. The molecular weights (\bar{M}_v) are OP 730,000, F-3 1,350,000, F-21 525,000, and F-35 160,000.

has been accumulating from experiments of other kinds: viscosity (5, 6, 8), diffusion (1), angular dissymmetry of light scattering (13, 23, 27) and depolarization of scattered light (12, 14).

For this investigation the poor solvents used were synthetic ones prepared by mixing solvent and nonsolvent. Recently Fox and Flory (16) have described the viscosity behavior of fractions of polyisobutylene in several solvents over a range of temperatures. For polyisobutylene, benzene and toluene are "poor" solvents, the values of $d[\eta]/d\theta$ being positive; and, as in our systems involving synthetic poor solvents, the temperature effect on intrinsic viscosity is much more marked with the high fractions. Other examples may be in the literature but, if so, they are few in number. Indeed comparatively few polymer-solvent systems exhibiting a marked increase of intrinsic viscosity with temperature have been reported (probably because of

a natural preference for good solvents and because most work has been done with polymers of relatively low molecular weight) and in nearly all such reports the polymer was unfractionated.

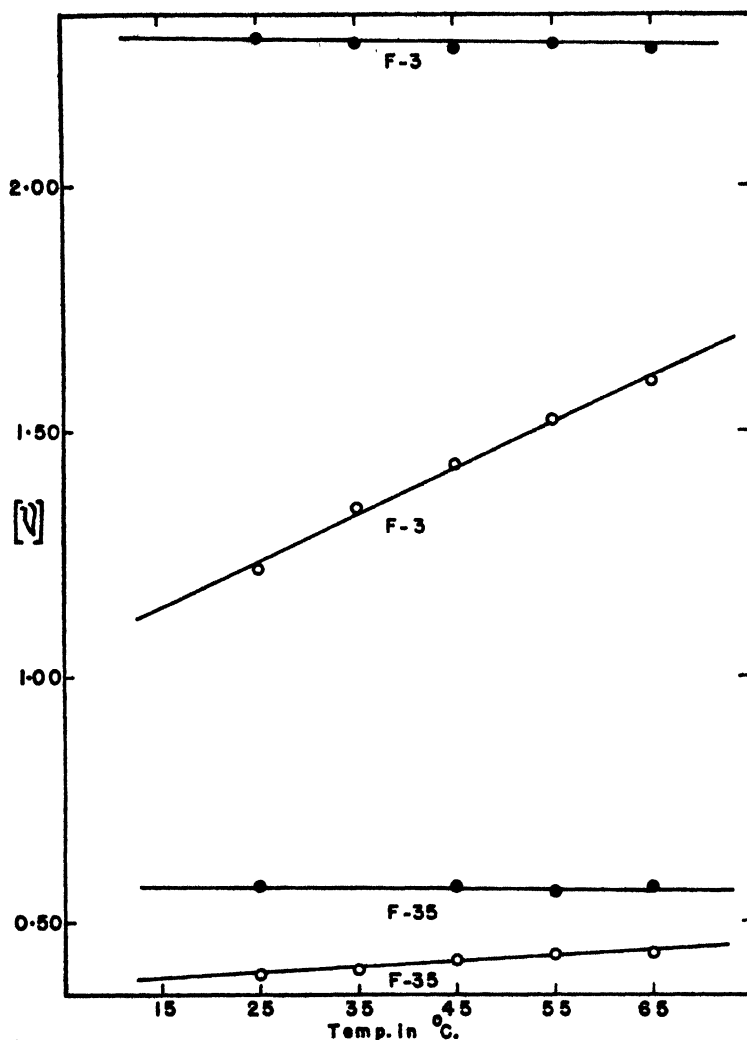


FIG. 4. Comparison of intrinsic viscosity-temperature behavior of high and low fractions of polystyrene in good and poor solvents.

—●—●— in toluene.
—○—○— in toluene-butanol.

The data of Fox and Flory for polyisobutylene also permit the calculation of values of $[\eta]_{\text{good}}/[\eta]_{\text{poor}}$, at 30° C., over a wide range of molecular weights with four combinations of the two poor solvents, benzene and toluene, and the two good solvents, cyclohexane and carbon tetrachloride (strictly these are "indifferent" solvents, for $d[\eta]/d\theta$ appears to be negligibly small). Again these values are greater for the higher fractions.

There is good reason to believe that the molecules of GR-S and of polystyrene (and of polyisobutylene) are much more flexible than those of, say, cellulose acetate or cellulose nitrate (22, 26). One would therefore expect lesser effects (particularly at lower molecular weights) with cellulose derivatives than those reported here, other things being equal. These effects are a consequence of the changing shape of the molecules in solution, and the shape assumed by the molecule depends in turn on its intensive flexibility as well as on its chain length, the nature of the solvent, the temperature of the solution, and the concentration. If in comparing different polymer-solvent systems these other things can be made "equal", it should be possible by determinations of intrinsic viscosity at various temperatures and in different solvents to obtain a measure of the relative flexibility of polymer molecules.

Acknowledgments

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THE EFFECT OF X- AND γ -RAYS ON AQUEOUS SOLUTIONS OF SODIUM THYMONUCLEATE¹

BY G. C. BUTLER²

Abstract

Aqueous solutions of sodium thymonucleate have been irradiated with X- and γ -rays and the effects have been assessed by measuring the changes in the viscosity of the solutions. The relations of change produced to total dosage, to the presence of protective agents, to concentration of solution, and to dosage rate indicate that the radiations act through the mediation of activated water. The relation of change produced to the state of the nucleate before irradiation suggests that irradiation initiates, by chemical action, a process that may thereafter proceed spontaneously.

Introduction

More information is needed about the chemical processes involved in the biological action of ionizing radiations; see Lea (7) and Allsopp and Catcheside (1). Since thymus type nucleic acid is a prominent constituent of chromosomes (11), although its precise biological function is not understood, it was hoped that an investigation of the chemical effects of ionizing radiations on this material might yield results of biological interest. It was also felt that the irradiation of nucleic acid might prove to be a useful tool for studying the macromolecular structure of the highly polymerized material. From a chemical point of view the use of radiations in such studies offers one unique advantage; it brings about changes in aqueous solutions without introducing any persistent foreign chemical.

An investigation with the above objects in view was conceived as falling into three parts, (a) a quantitative study of the changes produced by irradiation, (b) the identification of some of the processes involved, and (c) the study of the chemical alterations in the irradiated material. The present communication deals with phase (a) of the investigation.

A striking characteristic of solutions of highly polymerized sodium thymonucleate is their high degree of structural viscosity, and this is the property that was chosen for study in the present work. This property has the advantage that it readily lends itself to measurement with simple apparatus, and many workers have used intrinsic viscosity measurements as a measure of relative molecular weights. With such large and asymmetric particles as those formed by sodium thymonucleate in solution, measurements of intrinsic viscosity are not possible because a concentration-viscosity plot does not give a straight line and the slope cannot be estimated accurately at very low concentrations. Furthermore the apparent viscosity is markedly dependent on the rate of shear of the solution in the viscometer, and this effect is most noticeable with the low rates of shear obtained in the usual viscometers.

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For these two reasons it is impossible to obtain absolute viscosity values that may be related to particle size and shape. Consequently, most of the results of the viscosity measurements in the present work are expressed simply as the parameters of an equation relating rate of shear to shear stress. These parameters may be related to viscosity or structural viscosity under specified conditions.

It has been found that for a given polymer in solution the viscosity of the solution increased with the degree of polymerization of the solute. For this reason most workers assume that a reduction in the structural viscosity of solutions of a given sample of sodium nucleate is to be associated with a decreased axial ratio and a decreased molecular weight. In spite of the fact that the exact relation between these two properties and viscosity is not known it was felt that viscosity measurements were significant in a relative sense and could be used to obtain information about the nature of the radiation effect.

The criteria that have been formalized by Lea (7) have been used to determine if the action of the radiations is due to ionization within the affected material (direct action) or is brought about by the intervention of activated water molecules (indirect action). In order to identify such an indirect effect it is necessary to show that, (1) the shape of the curve relating yield to total dose is linear, (2) the presence of some foreign substance in the solution along with the material being irradiated results in a reduction of the yield due to irradiation, (3) above a certain critical concentration the absolute amount of change in the solute is independent of solute concentration. In the present work these three conditions have been met and in addition the results of an experiment with the effect of dosage rate on yield may be explained by an indirect action.

A number of samples of sodium thymonucleate with widely differing viscosity properties were subjected, in solution, to irradiation with radium γ -rays for identical periods and with identical dosage rates. It was found that the amount of change produced was directly proportional to the initial viscosity of the sample irradiated, and these results have led to some speculation about the nature of the depolymerization process.

During the course of this work two other reports on the same subject were made by Sparrow and Rosenfeld (13) and by Taylor, Greenstein, and Hollaender (14), respectively.

Materials and Methods

Viscosity Measurements

These measurements, except those in one experiment, were made with a modified Ubbelohde (15) suspended level type of viscometer having a capillary of radius 0.048 cm. and length 7.44 cm. The reservoir of the viscometer was a 5 ml. graduated pipette from which the solution was allowed to flow under the influence of gravity through the capillary, and the times of flow for successive 0.5 ml. portions were measured. All viscosity measurements were

made at $25 \pm 0.1^\circ \text{C}$. From the flow rates so obtained, the Hagenbach-Poiseuille formula, and the dimensions of the viscometer, rates of shear were calculated for shear stresses that varied from 32.6 to 87.0 dynes per cm^2 in the case of the above instrument.

For a 0.5% solution of sodium thymonucleate in the viscometer just described it was found that the rate of shear did not vary linearly with the shear stress. When the logarithms of the data are plotted as in Fig. 1 it

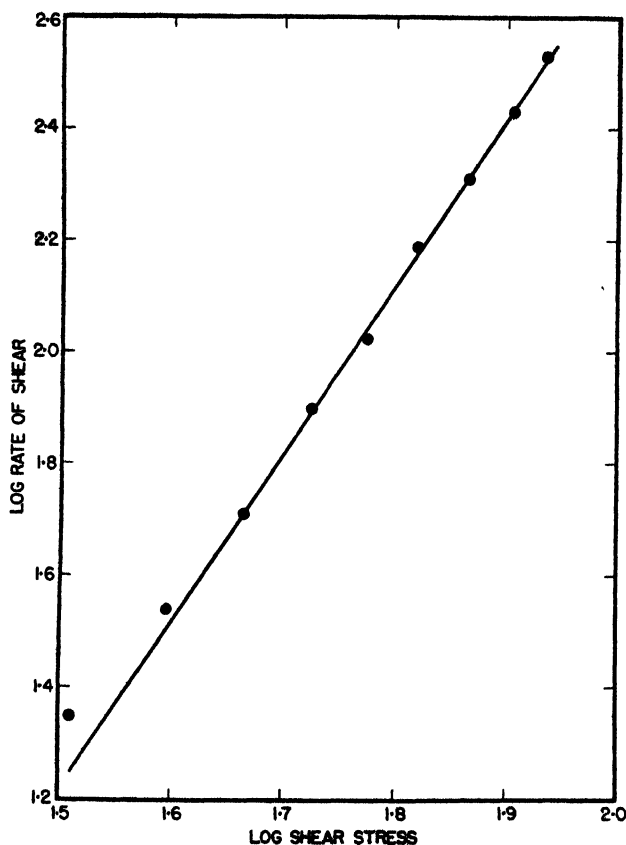


FIG. 1. Typical plot of log rate of shear against log shear stress derived from flow rate measurements with the Ubbelohde viscometer on a 0.5% solution of sodium thymonucleate.

becomes evident that the rate of flow of the solution through a capillary can be expressed by the equation $R = KS^m$, where R is the rate of shear, S is the shear stress, m is the slope of the straight line, and K is a constant. With the same apparatus it was found that this relation held for shear stresses as high as 170; however, it can be seen that there is some deviation from the linear relation at low rates of shear and this is probably due to factors that are not understood in the case of solutions with such a degree of anomalous viscosity.

The above equation has been found by Farrow, Lowe, and Neale (3), Wo. Ostwald (12), and others to apply to a variety of colloidal solutions, and it has been found convenient in the present work to summarize the results

obtained in viscosity measurements, in terms of values for K and m . In the case of solutions prepared from the same sample of "dry" nucleate at different times the variations in m were $\pm 5\%$; for different samples of the same solution of nucleate, determinations of m were reproducible to within $\pm 1\%$.

It was also found (Fig. 2) that the values of $\log K$ and m were proportional to the concentration of sodium thymonucleate in solution.

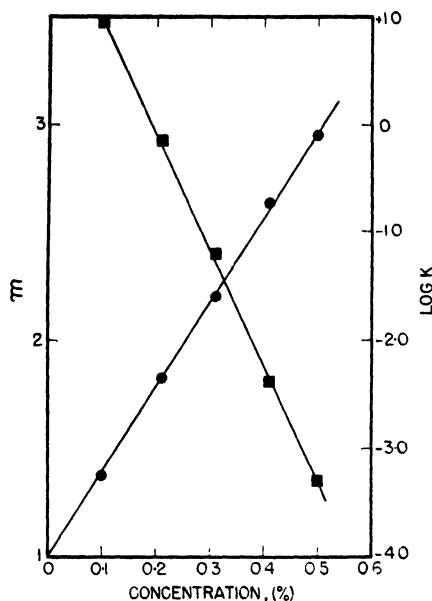


FIG. 2. ●—● change of m with change of concentration of sodium thymonucleate solution (left-hand ordinate scale).

■—■ change of $\log K$ with change of concentration of sodium thymonucleate solution (right-hand ordinate scale).

The investigation of the protective action of glucose, methanol, hydrogen peroxide, and irradiated nucleate was made using an Ostwald type of pipette (A.S.T.M. No. 100) containing 5.0 ml. of solution. This pipette was in a water bath at $25 \pm 0.1^\circ \text{C}$. during all measurements.

Sodium Thymonucleate and Thymonucleoprotein

As a result of considerable experience in the preparation of thymus nucleate it was found that the procedure of Mirsky and Pollister (10) consistently yielded more viscous preparations than did the method of Hammarsten (6). Consequently all the samples used in the present investigation were prepared by the former method, with some of the modifications suggested by McCarty and Avery (8) and Gulland, Jordan, and Threlfall (5).

Although great care was taken to work at low temperatures there was a great variability in the viscosity property of solutions of the final products. This is illustrated by the data in Table I, which are a representative selection from a much larger number of batches. Sodium citrate (0.01 M) was present in all solutions used in the preparation of Batches XI and XII and this seemed

TABLE I

VISCOSITY PROPERTIES OF DIFFERENT BATCHES OF SODIUM THYMONUCLEATE
(ALL MEASURED IN 0.5% SOLUTIONS)

Batch No.	m	$\log K$
<i>I c</i>	3.79	-5.18
<i>V</i>	2.18	-1.66
<i>VI</i>	1.54	-0.22
<i>VIII</i>	3.03	-3.42
<i>IX</i>	1.25	0.89
<i>X a</i>	2.92	-3.08
<i>X b</i>	2.70	-2.22
<i>X d</i>	1.49	0.04
<i>XI</i>	4.50	-6.36
<i>XII b</i>	3.26	-3.73

to yield a more viscous product. For all these batches the N : P ratios lay between 1.60 and 1.65 and the ratios of the extinction coefficient for aqueous solutions at 260 $m\mu$ to that at 230 $m\mu$ lay between 2.57 and 2.66. In spite of seven or eight emulsifications with chloroform until no more denatured protein appeared at the chloroform-water interface, all samples gave a faintly positive biuret test.

The thymonucleoprotein was prepared by the method of Mirsky and Pollister (10) and the final solution in 1 *M* sodium chloride was clarified by filtration through a loose mat of washed asbestos.

Irradiations

(a) With 200 kv. X-rays

The source of radiation in these experiments was a General Electric OX-220 X-ray machine operated at 200 kvp. and a tube current of 10 ma. The unfiltered beam was directed downward onto the sample, which was contained in a glass-stoppered weighing bottle inside a copper box with an aluminum lid 1 mm. thick; the interior of the box was kept at $25 \pm 1^\circ \text{C}$. Dosage measurements were made with a 100 r. Victorsen condenser chamber substituted as closely as possible in the position occupied by the sample. In this series of experiments the dosage rate was always 200 ± 10 r. per min.

(b) With 2 Mev. X-rays

For carrying out the irradiations at varying dosage rates the source of X-rays was a General Electric 2 Mev. X-ray machine that was operated at 2 Mev., and the tube current varied between 10 and 1000 μa . while the sample was kept at a fixed distance from the target. The X-ray beam was directed horizontally into a closed lead cylinder with walls 4 in. thick and an end 12 in. thick. To avoid uncertainties in dosage rate during the "working up" time of the machine, it was arranged to lower the sample into the beam, from a shielded position outside the cylinder, after the desired tube current had been established.

Solutions of sodium thymonucleate were irradiated in a closed polystyrene cell at temperatures ranging from 25° to 29° C. The cell was an exact replica of the ionization chamber used for dosage measurements, with the exception of some minor differences pertaining to the electrical measuring circuit. The dosage rates were thus measured by direct substitution.

The cylindrical ionization chamber was constructed of polystyrene with an adequate wall thickness to build up electronic equilibrium, and the wall was made conducting with Aquadag. The collecting electrode was a solid concentric cylinder of aluminum insulated with polystyrene and protected with a guard ring. The lower ends of both the collector and chamber were hemispherical and the effective chamber volume was 11.10 cc. The ionization current was measured by a null method, using a known high resistance; the voltage across the resistor was opposed by a measured e.m.f., the null point being determined with a sensitive electrometer. In all dosage rate measurements, care was taken to achieve saturation. From the current in the chamber and from careful measurements of chamber volume the dosage rates in roentgens were determined; these are given in Table V.

(c) *With radium γ -rays*

Two 1 gm. radium sources in monel metal containers having walls 1 mm. thick were in turn enclosed in a cylindrical aluminum holder; these provided the gamma radiation for these experiments. The solution to be irradiated was contained in a thin layer between two concentric cylinders of polystyrene, the inner cylinder being hollow so that the radium source could be inserted therein. All irradiations were carried out within a protecting lead shield at a temperature of $25 \pm 1^\circ$ C. The dosage rate was again measured by direct substitution; for the measurements the inner wall of the outer cylinder was coated with Aquadag and it served as the high voltage electrode while the outer wall of the inner cylinder was similarly treated and it served as the collector. The effective chamber volume was 9.79 cc. The ionization current in the chamber was measured by a null method as described above.

(d) *With Co^{60} γ -rays*

In one series of experiments approximately 2 c of radioactive cobalt (Co^{60}) was substituted for the radium source in the above arrangement.

Unless described otherwise the procedure for the irradiation of solutions of sodium thymonucleate was as follows. On the day of the experiment the dry sodium nucleate was weighed out and to it was added distilled water to give a solution of the desired concentration. The nucleate was dissolved by gentle agitation and when solution was complete (usually in one hour) the solution was divided into two portions, one being placed in the vessel for irradiation, the other being placed in a similar vessel to serve as a control. The control solution was stored, during the time of irradiation, at the same temperature as that at which the irradiation was carried out. Just before the end of the

irradiation the viscosity measurements were carried out on the control solution and immediately after the cessation of irradiation on the irradiated solution.

Taylor *et al.* (14) have reported that there was a gradual spontaneous decrease in the viscosity of their sodium thymonucleate solutions after cessation of irradiation and this phenomenon was also encountered in the present work. This makes it a difficult, and arbitrary, matter to select a time after irradiation for comparing viscosities. It was found that this behavior varied considerably from batch to batch of nucleate and that the fall, though slight, was quite rapid for a few minutes after irradiation but thereafter became much more gradual. The procedure adopted in all the present work was to carry out viscosity measurements at five-minute intervals until three consecutive sets of readings checked to within 1% and to take the mean of these as the recorded value. This relatively steady state was usually reached within 45 min.

Results

(a) Relation of Yield to Total Dose

The results of three separate experiments are plotted in Fig. 3. The data for each curve were obtained by irradiating samples of the same batch of

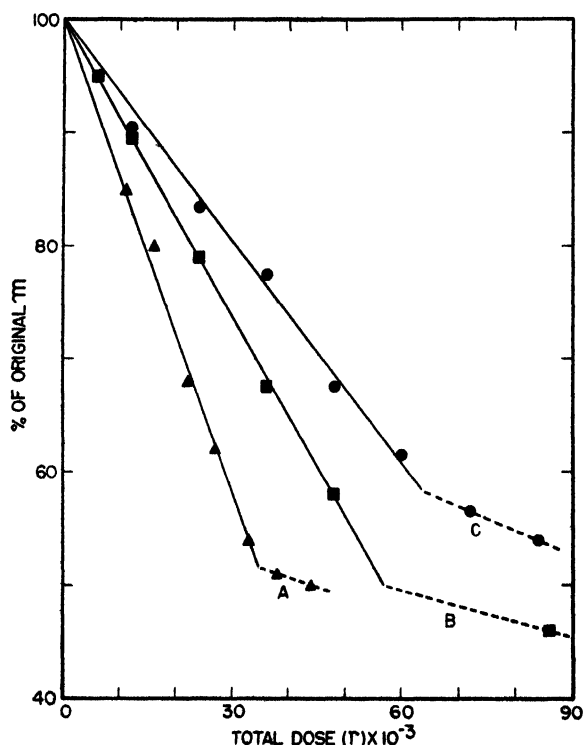


FIG. 3. Relation between viscosity and total dose of radiation for 0.5% solutions of sodium thymonucleate.

- A, \blacktriangle — \blacktriangle STN Batch VIII, radium γ -rays.
 B, \blacksquare — \blacksquare STN Batch VIII, 200 kv. X-rays.
 C, \bullet — \bullet STN Batch X a, 200 kv. X-rays.

sodium thymonucleate at the same intensity for varying lengths of time and measuring the difference between the viscosity properties of the control and irradiated samples.

The curves show that, when the decrease in m is used to measure the change effected, there is an approximately linear relation between dose and yield over a wide range of total dosage. There was a similar relation between $\log K$ and the total dose received. In each experiment the value of m at which the discontinuity in the curve appeared was approximately 1.5.

Another experiment was carried out under different conditions using a more dilute solution of sodium thymonucleate (0.05%), which had sodium chloride present in a concentration of 0.02 M . Samples of this stock solution were irradiated for various periods with Co^{60} γ -rays and the specific viscosities of the solutions were obtained from measurements with the Ostwald viscometer. The results of this experiment are plotted in Fig. 4.

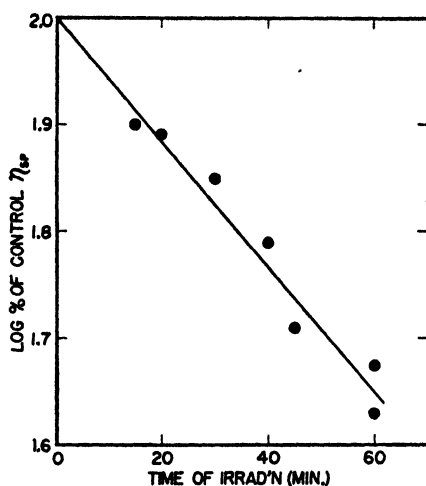


FIG. 4. The relation between viscosity and total dose of radiation. Solution (0.05%) of thymonucleate, Batch XXI in 0.02 M sodium chloride irradiated with Co^{60} γ -rays at 1.94 r. per sec.

The residual specific viscosity is close to being a linear function of total dose but the experimental values fit a straight line slightly better when they are plotted as in Fig. 4.

It therefore appears that the shape of the yield-dosage curve may depend on the experimental conditions used for obtaining it. The difference in the two results might be due to the strong gel formation in more concentrated solutions of thymonucleate in distilled water.

There can be two reasons for an exponential relation between yield and total dose; (a) the radiations act directly on the solute, and (b) the radiations produce activated water, which in turn reacts with the solute both before and after it has been altered by irradiation (2). The results of subsequent experiments showed that it was the second of these two factors that was responsible for any deviation from linearity of the yield-dosage curve.

(b) Effect of Protective Agents

Instead of measuring the protective effect of a foreign protein the nucleate was irradiated in its natural combination with histone. The solution that was irradiated was a 1% solution of thymonucleoprotein dissolved in 1 *M* sodium chloride; this solution had: N, 0.91 mgm. per ml. and P, 0.38 mgm. per ml. This phosphorus content was the same (within 5%) as those of the 0.5% solutions of sodium nucleate solutions used in other experiments. One hundred milliliters of the solution was prepared and stored at 5° C.; on each of three successive days two 8 ml. samples were removed to serve as the control and irradiated solutions, respectively. The results are summarized in Table II.

TABLE II

THE EFFECT OF PROTECTIVE AGENTS. IRRADIATION OF 1% SOLUTION OF THYMUS NUCLEO-PROTEIN IN 1 *M* SODIUM CHLORIDE WITH 200 KV. X-RAYS, 200 R. PER MIN.

Time of irradiation, hr.	<i>m</i>			log <i>K</i>		
	Control	Irradiated	Δm	Control	Irradiated	$\Delta \log K$
1	1.89	1.85	-0.04	-1.01	-0.92	0.08
2	1.87	1.78	-0.09	-0.87	-0.71	0.16
4	1.88	1.69	-0.19	-0.98	-0.50	0.48

It can be seen that the effect of the irradiation on the nucleoprotein solution is much less than that on a sodium nucleate solution. There are two possible explanations for this result. One is that the nucleic acid component, even though it was chemically altered by the irradiation, might be held in its original physical form by union with the histone. The other is that a large proportion of the activated water molecules reacted with the histone instead of with the nucleic acid. Although it was felt that the former explanation was unlikely it seemed clear that the effect of protective agents other than protein should be studied. Accordingly the protective actions of glucose, methanol, hydrogen peroxide, and irradiated sodium thymonucleate were measured.

The irradiated thymonucleate referred to was prepared as follows: Ten milliliters of a 0.5% solution of sodium thymonucleate, Batch XXI, 0.02 *M* with respect to sodium chloride was irradiated for 16 hr. with Co⁶⁰ γ -rays at 1.94 r. per sec. When a sample of this solution was diluted tenfold with 0.02 *M* sodium chloride solution it was found that its specific viscosity had been reduced from 0.94 to 0.08. This 0.5% solution, after irradiation, was used in the protective experiments.

The nucleate was dissolved in water, sodium chloride and a solution of the protective agent were added, and the volume of the solution was adjusted by the addition of water to give a solution containing 0.05% nucleate and 0.02 *M* sodium chloride. A number of such solutions were prepared each containing a different amount of the protective agent under study.

Samples of a solution containing any one concentration of protective agent were irradiated for various times with γ -rays from Co^{60} at a dosage rate of 1.94 r. per sec. The times of irradiation were chosen so that the longest irradiation reduced the specific viscosity of the solution more than 50%. Then, by plotting the percentage residual specific viscosity against time of irradiation, a curve similar to that in Fig. 4 was obtained. From such a curve the time of irradiation necessary to reduce the specific viscosity by 50% ("half-dose", D_2) could be obtained by interpolation. These "half-doses" for a number of different concentrations of protective agent were plotted against concentration of protective agent. Fig. 5 is the plot obtained for

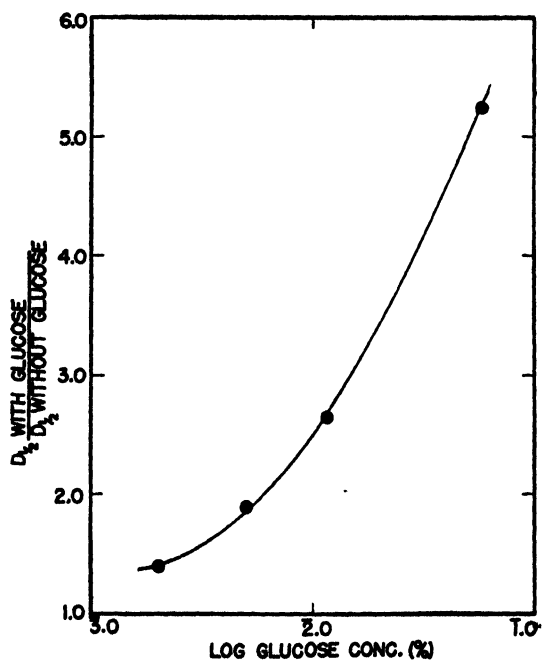


FIG. 5. The effect of glucose on "half-dose". Solution (0.05%) of thymonucleate, Batch XXI in 0.02 M sodium chloride irradiated with Co^{60} γ -rays at 1.94 r. per sec.

glucose. From such plots the concentration of protective agent necessary to double the "half-dose" was read off. These are the concentrations that give 50% protection of the nucleate against the action of activated water and that are recorded in Table III.

Hydrogen peroxide had no protective or enhancing action in a concentration of 0.3%.

Results such as these make it possible to compare the relative affinities of activated water for different substances in solution.

(c) Effect of Concentration of the Solute

Sodium thymonucleate, Batch V, in 0.25, 0.50, and 1.0% aqueous solutions was irradiated with 200 kv. X-rays, the total dose being 12,000 r. The results are summarized in Table IV.

TABLE III

THE RELATIVE EFFECTIVENESS OF PROTECTIVE AGENTS. SOLUTION OF BATCH *XXI* SODIUM THYMONUCLEATE (0.05%) IN 0.02 *M* SODIUM CHLORIDE IRRADIATED WITH Co^{60} γ -RAYS AT 1.94 R. PER SEC.

Protective agent	Concentration for 50% reduction in yield
Glucose	0.31 mM.
Methanol	0.69 mM.
Irradiated sodium thymonucleate	0.042%

TABLE IV

THE EFFECT OF CONCENTRATION ON YIELD. BATCH *V* SODIUM THYMONUCLEATE IRRADIATED WITH 200 KV. X-RAYS FOR ONE HOUR AT 200 R. PER MIN.

Concentration at irradiation, %	Conc'n at viscometry, %	<i>m</i>			Yield*
		Control	Irradiated	Δm	
0.25	0.25	1.81	1.68	-0.13	7.2
0.50	0.50	2.23	2.07	-0.16	7.2
1.0	0.50	2.24	2.14	-0.10	8.9

$$* \text{Yield} = \% \text{ reduction in } m \times \frac{\text{conc'n. at irradiation}}{\text{conc'n. at viscometry}}$$

It was not feasible to use a greater range of concentration because of the inconvenience of measuring the viscosity property of solutions that were either too concentrated or too dilute. But within the range of concentration studied (fourfold) it is apparent that for a given dose the absolute yield did not vary greatly. In order to study the effect of solute concentration further, a sample of Batch *VIII* was irradiated in the "dry" state. Two 50 mgm. samples of this sodium nucleate were weighed and one sample was placed in each of two 10 ml. volumetric flasks. One sample received 24,000 r. of 200 kv. X-rays in two hours after which 8 ml. of water was added to each flask and the nucleate dissolved by gentle agitation. The volumes were adjusted to 10 ml. with water, the solutions thoroughly mixed, and the viscosity behavior of each solution was measured as usual. The values obtained were as follows:

	<i>m</i>	log <i>K</i>
Control	3.26	-4.95
Irradiated	3.21	-4.85

The effect of 24,000 r. of X-rays was therefore negligible in the absence of water. The results of these two experiments provide further evidence that the main effect of X-rays on nucleate solutions is mediated by the water in which the nucleate is dissolved.

(d) Effect of Dosage Rate

Samples of sodium thymonucleate, Batch X b, in 0.5% solutions were irradiated with 20,000 r. of 2 Mev. X-rays at rates varying between 1.6 and 124 r. per sec. The viscosity changes resulting from the irradiations are summarized in Table V.

TABLE V.

EFFECT OF DOSAGE RATE ON YIELD. IRRADIATION OF SODIUM THYMONUCLEATE, BATCH X b, IN 0.5% SOLUTION WITH 2 MEV. X-RAYS, TOTAL DOSE 20,000 R.

Current in X-ray tube, ma.	Dosage rate, r./sec.	Control solution		Irradiated solution		Δm
		<i>m</i>	log <i>K</i>	<i>m</i>	log <i>K</i>	
0.01 "	1.6 "	2.68	-2.70	2.21	1.65	-0.47
		2.62	-2.62	2.11	-1.43	-0.51
0.03 "	4.5 "	2.65	-2.63	2.21	-1.63	-0.44
		2.66	-2.62	2.24	-1.71	-0.42
0.10 "	12.9 "	2.72	-2.78	2.35	-1.96	-0.37
		2.70	-2.70	2.33	-1.89	-0.37
1.0 "	124 "	2.69	-2.69	2.29	-1.87	-0.40
		2.65	-2.65	2.26	-1.80	-0.39

During these experiments there arose two technical difficulties that should be mentioned. Firstly, it was very difficult to control the tube current at a constant value of 0.01 ma. and this difficulty probably explains the poor agreement between the two values of Δm recorded for the first experiment. Secondly, in order to carry out the irradiation at 124 r. per sec. it usually required about 30 min. to develop a current of 1 ma. in the X-ray tube, and during this period the sample, in its position just outside the lead cylinder enclosing the X-ray beam, probably received an appreciable irradiation before it was placed in the beam. Therefore in the last experiment the total dose was probably greater than 20,000 r. and this is the only reason that can be given for the unexpectedly high yield obtained with the highest dosage rate.

From the results of the first three experiments it can be seen that there is a small and regular decline in yield as the dosage rate is increased from 1.6 to 12.9 r. per sec. This finding can be most readily explained as follows. Suppose that on irradiation water molecules are activated by being converted into two kinds of reactive fragments, *A* and *B*, and that *A* reacts with the dissolved nucleate to alter its structure or with *B* to re-form water. Nucleate and *B* will therefore compete for the available *A*. Under the conditions of the experiment just described increasing the dosage rate will increase the concentration of *B* while the concentration of nucleate remains constant so that a greater proportion of *A* will be reacting with *B* at high dosage rates than at low ones. This could account for the reduction in yield with increasing dosage rates but since the reduction in yield is slight the reaction of *A* with *B* may be regarded as small in comparison with the reaction of *A* with nucleate.

(e) *Effect of Condition of the Nucleate before Irradiation*

Eight different samples of sodium thymonucleate in 0.5% solutions received identical irradiations with radium γ -rays; the results are presented in Table VI. With the exception of the two samples with the lowest viscosities

TABLE VI

VARIATION OF YIELD WITH DIFFERENT SAMPLES. SOLUTIONS (0.5%) OF SODIUM THYMONUCLEATE IRRADIATED FOR TWO HOURS WITH RADIUM γ -RAYS AT 91 R. PER MIN.

Batch No.	m (for control sol'n.)	$-\Delta m$ (due to irradiation.)	$\frac{-\Delta m}{m - 1}$
<i>I c</i>	3.79	0.73	0.26
<i>V</i>	2.18	0.31	0.26
<i>VI</i>	1.54	0.10	0.19
<i>VIII</i>	3.03	0.45	0.22
<i>X a</i>	2.92	0.45	0.24
<i>X d</i>	1.49	0.04	0.08
<i>XI</i>	4.50	1.00	0.29
<i>XII b</i>	3.26	0.58	0.26

(*VI* and *X d*) the values in the last column are fairly constant, showing that the yield for a given amount of irradiation is proportional to the degree of anomaly of the viscosity of the solution that is irradiated.

It is interesting to note that the initial values of m for 0.5% solutions of samples *VI* and *X d* are near 1.5 where it was noted the discontinuities occurred in the curves of Fig. 3.

The results obtained with the remaining six samples can most easily be explained by assuming that the initial value of $m - 1$ is directly proportional to the degree of polymerization or that samples with the highest values of $m - 1$ show the greatest departure from some unpolymerized state. It would then be possible to obtain the results recorded in Table VI if the depolymerization proceeded in two stages as follows. (a) A certain number of chemical events take place in the macromolecule and initiate the process of depolymerization. These chemical events are probably the reaction of activated water with bonds in the macromolecule and they could be the same for all samples. (b) Each macromolecule in which this initial process has happened then depolymerizes spontaneously from its initial state to an unpolymerized state.

If process (b) were slow then the above scheme would provide an explanation for the slow spontaneous decrease that takes place in the viscosity of irradiated solutions after cessation of the irradiation.

(f) *Quantitative Considerations*

It is of some interest to estimate the number of active radicals that must react with unit weight of thymonucleate to produce, say, a 50% reduction in the specific viscosity of a solution. From Fig. 4 it can be seen that 5,900 r.

of γ -rays will reduce the specific viscosity of a 0.05% solution of batch *XXI* thymonucleate by 50%. Miller (9) has shown that 1000 r. of γ -rays will bring about the oxidation of 19.5 μ M. per liter of ferrous ions in an air-saturated solution. Dewhurst and Krenz (private communication) have found that, in an oxygen-free solution, 5 μ M. per liter of ferrous ion is oxidized per 1000 r. The fourfold greater yield in the presence of oxygen is to be explained by oxidizing agents formed on the interaction of activated water and oxygen. It may thus be assumed that 1000 r. of γ -rays produces 5 μ M. of active radicals of one kind per liter.

Irradiation of thymonucleate solutions gave the same reduction in viscosity in the presence and in the absence of oxygen; so it follows that 59 μ M. of active radicals react with one gram of sodium thymonucleate to reduce the specific viscosity by 50%. Similar calculations based on similar data for Batch *XIII* thymonucleate give a corresponding value of 81 μ M. per gram. Assuming that one gram of thymonucleate can react with twice these amounts of active radicals, one obtains a value of 8500 for the effective molecular weight of Batch *XXI* and 6200 for Batch *XIII*.

These values for the number of active radicals reacting may be in error because it is assumed that one active radical of one kind, produced by the action of the γ -rays on water, (i) oxidizes one ferrous ion and, (ii) reacts productively with thymonucleate. It is difficult to assess the validity of the first assumption which leads to a minimum estimate of the number of active radicals produced by the radiations. The second assumption is a maximum estimate; it must be too high by at least 30% because it was shown in Section (b) that irradiated nucleate had an affinity for activated water equal to that of the unirradiated material.

In spite of their uncertainty, calculations of the sort just made seem to be more informative than estimates of ionic yield for which one has to assume an effective molecular weight. Any estimate of ionic yield also involves the assumption that one ion pair is produced in 1 ml. of water by the absorption of 32 e.v. of energy from the radiations; this number has never been settled by experiment. Using a molecular weight value of one million (that obtained in some sedimentation studies) for sodium thymonucleate, one obtains an ionic yield of 0.02 for the viscosity reduction of Batch *XXI* by irradiation.

Discussion

The conclusions to be drawn from each experiment have been given in the previous section. It remains to consider their interpretation.

A correlation of the results is made difficult by the fact that the material under study has an unknown constitution and an uncertain molecular weight. It seems most probable that the reduction in viscosity by irradiation results from an alteration of inter- or intra-molecular linkages in the macromolecules but there is no evidence indicating the nature of these linkages. As a result

of their study of the reduction in the viscosity of sodium thymonucleate solutions on treatment with acid or alkali, Gulland and Jordan (4) suggested that the linkages affected were hydrogen bonds between amino and hydroxyl groups. Such bondings, if they exist, might be the site of action of the ionizing radiations, but this or any other theory of the site of action is purely speculative at present.

Whatever is the point of attack of the ionizing radiations on the nucleate, there seems very little doubt, as a result of this investigation, that the attack is mediated by activated water molecules and that direct ionization in the nucleate molecules has by comparison a negligible effect.

It is doubtful if the results obtained so far in this work have any direct implications for biology. There is no way of knowing what is the native physical state of the nucleic acid in the cell nucleus. It seems to be implied in all communications dealing with the isolation of thymus type nucleate that the greater the degree of anomalous viscosity of the isolated product the less degraded it is and therefore the more does it resemble its original state in the living cell. One must always consider the possibility, however, that the high degree of structural viscosity may be brought about by the isolation process.

The doses required to produce a measurable effect on the sodium nucleate are far greater than those required to bring about striking changes in the nuclei of living cells, but this is not surprising in view of the very large number of individual chemical events that would be necessary to give rise to a measurable chemical or physical change in the material. From a strictly biological point of view it would be much more interesting to irradiate a nucleic acid such as the pneumococcus-transforming principle of McCarty and Avery (8), which has a biological action in very small amounts. It is possible that with such a material a measurable alteration could be obtained with much smaller doses of radiation.

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MEMBRANE EQUILIBRIA, THE GIBBS-DALTON LAW AND THE ENTROPY OF MIXING¹

BY E. A. FLOOD AND G. C. BENSON

Abstract

When two pure fluids whose pressures are p_1 and p_2 , respectively, are separated by means of semipermeable membranes from a mixture of these fluids, and under equilibrium conditions the pressure of the mixture is P , then the net pressures sustained by the diaphragms are $P - p_1$ and $P - p_2$, respectively. The assumption that these net pressures are p_2 and p_1 , respectively, is equivalent to assuming the Gibbs-Dalton law, namely $p_1 + p_2 = P$. It is shown that the Gibbs-Dalton law when applied to fluids that are not ideal gases leads to consequences which are entirely contrary to experience and that as applied to ideal gases it has neither an experimental nor theoretical thermodynamic basis. It is shown that the Gibbs-Dalton law is only a special case of Dalton's law and that the classical thermodynamic paradox in the entropy of mixing of ideal gases is based on the erroneous assumption that the Gibbs-Dalton law necessarily holds when Dalton's law holds. It is shown that when two ideal gases obey Dalton's law of mixing, it is thermodynamically quite possible for the equilibrium pressure of one pure gas to be increased while that of the other is decreased, as well as the more familiar case of "chemical reaction", where the equilibrium pressures of both are decreased. It is shown that there is no purely thermodynamic requirement that different kinds of molecules in mixtures of ideal gases shall have the same mean translatory kinetic energy. The ideas underlying membrane equilibria are discussed in some detail. Some general condition equations which must be met are given, together with a few explicit solutions of these equations for special simple cases.

I. Introduction

All fluids which are appreciably different from one another react with one another to a greater or lesser degree, when allowed to intermix. The extent to which such reaction occurs often depends on highly specific subtle factors inherent in the natures of the fluids. Usually such specific factors are not included in the statistical models of the fluids concerned. The omission of these factors introduces uncertainties in the theoretical treatment of the mixing of the statistical models and these uncertainties lead, in turn, to uncertainties in the statistics of mixtures of even the simplest of statistical models of thermodynamic fluids. Before considering statistical or mechanical details of such models it is necessary to ensure that the model fluid mixture fulfill two requirements. The first and absolutely essential requirement is that the mixing behavior of the fluid models be thermodynamically possible, otherwise the terms "temperature", "energy", etc., as applied to the models are practically meaningless. The second requirement is that the behavior of the model be physically reasonable, in the sense that it should not be in conflict with well established experience, and should, if possible, be free from paradoxes.

This paper presents some thermodynamic and physical considerations concerning the mixing of fluids, special emphasis being placed on the mixing of

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ideal gases. While this subject has been discussed at length in the scientific literature, there are one or two points that appear to have been overlooked, to which attention is invited in the following pages.*

Membrane Equilibrium, the Entropy of Mixing, and the Gibbs-Dalton Law

"Membrane equilibrium", "the entropy of mixing," and the "Gibbs-Dalton law" are three commonly used expressions denoting ideas which are closely associated with one another and with the thermodynamics of fluid mixtures.

If we imagine a given fluid to be separated by means of a semipermeable membrane from a mixture of the given fluid and other fluids and we suppose that the membrane allows the given fluid to pass through it quite readily but prevents passage of the other fluids, and we now suppose that the other fluids in the mixture literally *act as a vacuum* to the given fluid, we must conclude that the concentration of the given fluid will be the same on either side of the membrane under equilibrium conditions. If, however, there is any sort of thermodynamic interaction between the given fluid and the other fluids in the mixture, then under equilibrium conditions there will be, in general, a difference between the concentrations of the given fluid on either side of the membrane. This difference in concentrations or molar densities will constitute a measure of the degree of thermodynamic interaction of the given fluid with the others in the mixture.

It might at first be thought that a fluid could never act as a vacuum to another fluid, but when we consider the possibilities of expanding different, very dilute gases into one another through semipermeable membranes, one is inclined to think that there should be a very general class of cases where volumes of different fluids act as empty spaces to one another, in spite of the paradoxical fact that volumes of the same fluid cannot act as empty spaces to one another under any finite circumstances, however dilute they may be, however closely they may approach a vacuum.

The paradoxical nature of these ideas has been set forth by many writers, especially by Gibbs in connection with the "entropy of mixing" and leads to the well known Gibbs paradox. We shall see, however, that the paradox is, perhaps, more imaginary than real and owes its origin to unwarranted assumptions concerning equilibrium pressures across semipermeable membranes.

The "entropy of mixing" of fluids, as the expression is generally used, refers to the entropy change, if any, which accompanies the removal of a partition separating two fluids which are under the same pressure and which have the same temperature. It may be taken as axiomatic that if the fluids have the same

* While the literature dealing with this classical subject is so voluminous that it is impractical to provide anything like a complete bibliography, we would like to acknowledge a few of the sources to which we are most indebted.

These are: *The Collected Work of Willard Gibbs and Donnan and Haas's valuable commentary thereon; the series of scientific papers on this subject by Louis Gillespie; the papers of Beattie and of Guggenheim on the thermodynamics of gas mixtures; the standard thermodynamic textbooks, notably those of Lewis, Epstein, and Guggenheim.*

temperature and pressure, and surface and external forces are negligible, no entropy change will occur on removal of the partition, if the fluids are identical. However, if the fluids are not identical it is practically impossible to predict from a priori considerations whether a finite entropy change will occur or not. Neither very close similarity nor very great differences in the thermodynamic and physical properties will enable one to make any accurate a priori calculations of the entropy of mixing. If the two fluids are not identical and are miscible in the sense that a uniform distribution of material throughout the whole volume is rapidly attained after removal of the partition, usually an entropy change will occur. Usually there will also be a change in the energy of the system and in the value of (PV) , and hence, a change in the values of the thermodynamic functions H , A , and F .^{*} If a chemical reaction occurs and $(-\Delta F)$ is large, usually $(-\Delta E)$ is also large, but $(-\Delta F)$ may be large for reactions where (ΔE) and $\Delta(PV)$ are both practically zero. In such cases the large value of $(-\Delta F)$ for the reaction is due to a large, "entropy of mixing" or "entropy of reaction". In cases where (ΔE) and $\Delta(PV)$ are zero and ΔS is comparatively small it might be very difficult to distinguish between "reaction", "solution", and mere "mixing". If we consider that the mere fact that the fluids are different necessarily implies a minimum entropy of mixing, considerably greater than zero, we might find ourselves in difficulties in cases where the entropy change of the process was actually negative, as it is in some reactions. It would be more logical to assume that when no reaction occurs ΔE , ΔH , ΔP , ΔA , ΔF , and ΔS are all zero, as would be the case were the fluids identical. Thus we might be inclined to regard the classical entropy of mixing as an entropy of reaction. When looked at from this point of view, in cases where ΔE and $\Delta(PV)$ are zero, we might expect ΔS to vary from zero through the classical value to very large values depending on the nature of the fluids. Certain types of these reactions might be regarded as chemical reactions, but there will be cases where there is no sharp line of demarcation between "chemical reaction", "solution", and "mixing reaction". This view has at least the merit of logical continuity of ideas.

It seems unreasonable if not altogether illogical to suppose that the "mixing reaction", the "entropy of mixing", in the case of different ideal gases cannot be less than the classical entropy of mixing no matter how small the difference between the fluids might be. Surely, if the two fluids are inert monatomic gases which differ only in the fact that their nuclei have different half lives, say 10^{10} and 10^{11} years, respectively,—surely it would seem that the "entropy of mixing" would not be the same as if the gases had quite different atomic weights, or were altogether different substances? It seems perfectly clear that nothing resembling a semipermeable membrane is capable of separating, *reversibly*, fluids whose only difference lies in the relative stabilities of the nuclei of their atoms. Is there not a fallacy in postulating the existence of a semipermeable membrane such that the equilibrium across it requires

^{*} Lewis symbols, cf. p. 992 of this paper.

the concentrations of the inert gas to be the same on either side, irrespective of the presence on one side of a second inert gas which differs from the first gas only in that the nuclei of its atoms are slightly more or less stable? Surely we must know the equilibrium conditions before we postulate the hypothetical membrane? The equilibrium condition has, really, little to do with the semipermeable membrane. The membrane is merely a simple device used for carrying out pencil and paper operations between systems in equilibrium. The paradox that the entropy of mixing of different ideal gases is independent of the nature of the gases and independent of the degree of difference of these gases, is a result of assuming that the pressure of an ideal gas mixture is equal to the sum of the equilibrium pressures of the pure gases when separated by semipermeable membranes from the mixture.* This assumption has been shown by Gibbs to be exactly equivalent thermodynamically to the assumption that each gas is as a vacuum to the other gas, irrespective of the equations of state. The question as to the entropy of mixing of fluids is thus reduced to the practical questions: Do different fluids usually act as empty spaces to one another? Do different ideal gases generally act as a vacuum to one another?

The view that different gases act as a vacuum to one another is attributed to Dalton by Lord Rayleigh (4). It is sometimes thought that Dalton's law, and the notion that gases act as empty spaces to one another, amount to the same thing. But that this is far from the case is obvious when we consider that Dalton's law can be applied in the case of identical ideal gases, while no gas can act as a vacuum to itself or to another portion of the same gas at the same pressure. Gibbs (1, p. 155) summarized the views of his time concerning fluid mixtures as follows "The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential". Gillespie (2) has called this the Gibbs-Dalton law. Gibbs (1, p. 157) showed that this law was thermodynamically equivalent to the statement that "every gas acts as a vacuum to every other gas" irrespective of the equations of state of the pure gases. Dalton's law is, of course, quite different, namely, "the pressure exerted by a mixture of gases is equal to the sum of the pressures which each gas would exert, if it occupied the space alone". One would not expect this law to be valid for gases which depart appreciably from the perfect gas laws. When confined to perfect gases, Dalton's law is obviously applicable when the gases are identical, whereas the Gibbs-Dalton law is clearly not applicable when the gases are the same. If the Gibbs-Dalton law is generally valid for different ideal gases, the paradox in the entropy of mixing is almost inescapable† but if the Gibbs-Dalton law is not generally valid, the paradox is largely imaginary.

* Cf. footnote on p. 1005.

† Statistical considerations do not in any sense "resolve" the paradox but rather tend to emphasize the self-contradictory nature of the ideas involved. Perhaps the essential question is: Can fluids be identical thermodynamically but differ with respect to nonthermodynamic processes?

In what follows we shall derive the conditions for equilibrium across semi-permeable membranes. We shall examine any general solutions that may be obtained in order to ascertain whether there is any thermodynamic reason why ΔS should have some positive minimum where ΔE and $\Delta(PV)$ are zero for such mixing processes as we have discussed. We shall enquire as to whether the Gibbs-Dalton law has any theoretical validity based on thermodynamic considerations or any physical validity based on experience in the behavior of fluid mixtures generally.

II. Membrane Equilibrium

Thermodynamic Relations

The general condition that changes in the thermodynamic variables of a system shall be reversible is that the heat received by the system during such changes shall be equal to the changes in the energy of the system plus the maximum work (if a finite maximum exist) which the system can do against external forces during such changes. This is virtually Carnot's condition for reversibility of a heat engine and leads to the following well known conditions for thermodynamic equilibrium with respect to various specified variations of a given system:

$$(\delta E)_{S,V,X}, (\delta H)_{S,P,X}, (\delta A)_{T,V,X}, (\delta F)_{T,P,X} \geq 0$$

and,

$$(\delta S)_{E,V,X} \leq 0,$$

where E is the energy, S the entropy, V the volume, T the temperature, P the pressure, $H = E + PV$, $A = E - TS$, $F = H - TS$, and X represents other co-ordinates of the system which are to be held constant during the variation. All of these conditions are equivalent. If the equilibrium is to be a neutral equilibrium with respect to specified changes and if these changes are to be reversible, the above variations must vanish.

When a system consists of various parts which may be transformed into one another, the most generally useful condition of equilibrium with respect to such transformations is, $(\delta F)_{P,T,X} = 0$, since in such transformations we usually assume that the *measurable variables* describing the state of two parts, namely, their temperatures and pressures, are to be held constant while only the various masses change. Hence for a process of transformation of two separate systems into a single system containing the same matter, where the temperatures and pressures of each separate system are to remain constant throughout the process (if such a process exist), the condition that it shall be reversible is that,

$$F_{12} = F_1 + F_2,$$

where the system having the free energy F_{12} contains the same matter as in the separate systems having free energies F_1 and F_2 respectively. While this condition for equilibrium is perhaps the most generally useful, when we

wish to determine an equilibrium with respect to the distribution of matter between constant volumes, the appropriate equilibrium condition is that,

$$(\delta A)_{T,V,X} = 0.$$

This condition for equilibrium is particularly well adapted to the determination of the distribution of a matter between volumes separated by means of semipermeable membranes.

We shall now consider some problems associated with such membranes. Of course, in any case where different bodies are assumed to be in thermal contact, the additional requirement for equilibrium is that the temperatures be the same.

Let the following diagram represent a container divided into three volumes, v_{1e} , v_{2e} and V by partitions (1) and (2).

p_{1e}	P	p_{2e}
n_1	n'_1	
u_1	x	
	n'_2	n_2
	y	u_2
v_{1e}	V	v_{2e}
1		2

FIG. 1

Let partition (1) be permeable only by the first fluid and let there be n_1 and n'_1 moles of this first fluid contained respectively in v_{1e} and V . Similarly partition (2) is to be permeable only by the second fluid and there are to be n_2 and n'_2 moles respectively in v_{2e} and V . The temperature is to be uniform throughout the three volumes. The pressures exerted against the impermeable walls of each volume are to be p_{1e} , P , and p_{2e} respectively, and are to be uniform throughout each separate volume but are not necessarily equal. We shall assume, that an equilibrium can exist under these circumstances and that the volumes v_{1e} and v_{2e} are so chosen that $n_1 = n'_1$ and $n_2 = n'_2$.

We shall also assume that an equation of state $p = f(n, V, T)$ exists where f is homogeneous and of zero degree in n and V , and that surface effects may be neglected. Then putting $u = \frac{n}{V}$ we may write $f(n, V, T) = g(u, T)$, since g cannot contain n explicitly. Hence $p = p(u, T)$ or at constant temperature $p = p(u)$. We shall find it convenient in what follows to use equations of state of this form.

Referring to Fig. 1, if we let $u_1 = n_1/v_{1s}$, $u_2 = n_2/v_{2s}$, $x = n'_1/V$, and $y = n'_2/V$, evidently relations exist as between u_1 , u_2 and x and y . We enquire as to what may be deduced concerning these relations.

Let us write,

$$u_1 = xf_1(x, y), \quad u_2 = yf_2(x, y). \quad (1)$$

Evidently f_1 and f_2 are subject to the following boundary conditions:

$$f_1(x, y \pm 0) = f_2(x = 0, y) = 1. \quad (2)$$

$$xf_1(x, y) = 0, \text{ when } x = 0,$$

$$yf_2(x, y) = 0, \text{ when } y = 0.$$

These are necessary boundary conditions imposed on f_1 and f_2 by the physical nature of the assumed system. However, if the form of the equations of state and the values of the variables permit more than one concentration for a given equilibrium pressure, a variety of relations may exist between u_1 and x even when $y = 0$. If, for example, $p = p_1(u_1) = p_1(u'_1)$, where $u'_1 > u_1$, then assuming only that the pressures and temperatures are uniform, the value of u may have any value from u_1 to u'_1 . Hence a variety of relations between u_1 and x may be consistent with equilibrium. Here we shall assume that u_1 and x refer to the smallest of these values if more than one value is consistent with equilibrium. We shall discuss these boundary conditions more fully after presenting some of the necessary relations which must subsist between the functions f_1 and f_2 .

For a neutral equilibrium to exist between the fluids contained in v_{1s} and v_{2s} and the mixed fluid in V , the temperature of each must be the same and the variation in the Helmholtz free energy, δA , resulting from a change in the distribution of matter as between the constant volumes must vanish. If the distribution of the first fluid between the volumes v_{1s} and V is to be independent of the presence or absence of the system v_{2s} , we may write

$$\delta A = \left(\frac{\partial A_{12}}{\partial n'_1} \right)_{T, V, n_2} \delta n'_1 + \left(\frac{\partial A_1}{\partial n_1} \right)_{T, v_{1s}} \delta n_1 = 0$$

and assuming $n'_1 + n_1 = \text{constant}$, we get,

$$\left(\frac{\partial A_{12}}{\partial n'_1} \right)_{T, V, n_2} = \left(\frac{\partial A_1}{\partial n_1} \right)_{T, v_{1s}}$$

$\left(\frac{\partial A_{12}}{\partial n'_1} \right)_{T, V, n_2}$ is, of course, Gibbs thermodynamic potential of the first component in the mixed system. Representing this quantity by μ'_1 , and letting μ_1 represent the thermodynamic potential of the same component in the system v_{1s} , which contains only this substance, the equilibrium condition becomes,

$$\mu'_1 = \mu_1$$

And similarly,

$$\mu'_2 = \mu_2$$

To every system having a uniform pressure and temperature throughout, whether homogeneous or not, an equation of the form of Gibbs (97)

$$VdP = SdT + n_1d\mu_1 + n_2d\mu_2 \dots \dots \dots$$

is applicable. Thus for the mixed system we have,

$$VdP = SdT + n'_1d\mu'_1 + n'_2d\mu'_2,$$

and for the first system,

$$v_{1s}dp_{1s} = S_1dT + n_1d\mu_1,$$

while for the second system,

$$v_{2s}dp_{2s} = S_2dT + n_2d\mu_2.$$

Since,

$$\mu'_1 = \mu_1, d\mu'_1 = d\mu_1,$$

$$\mu'_2 = \mu_2, d\mu'_2 = d\mu_2,$$

and,

$$n'_1 = n_1, n'_2 = n_2,$$

and T is constant, after eliminating $n_1d\mu_1$, etc., we get the equivalent fundamental equations,

$$VdP = v_{1s}dp_{1s} + v_{2s}dp_{2s} \quad (3)$$

and,

$$\begin{aligned} dP &= \frac{v_{1s}}{V} dp_{1s} + \frac{v_{2s}}{V} dp_{2s} \\ &= \frac{x}{u_1} dp_{1s} + \frac{y}{u_2} dp_{2s}, \end{aligned} \quad (4)$$

where p_{1s} and p_{2s} and hence u_1 and u_2 may be regarded as independent variables, or we may regard x and y as independent variables*. Choosing x and y as independent variables we get,

$$\begin{aligned} dP &= \frac{x}{u_1} \frac{dp_1}{du_1} \left[\frac{\partial u_1}{\partial x} dx + \frac{\partial u_1}{\partial y} dy \right] + \frac{y}{u_2} \frac{dp_2}{du_2} \left[\frac{\partial u_2}{\partial x} dx + \frac{\partial u_2}{\partial y} dy \right] \\ &= \left[\frac{x}{u_1} \frac{dp_1}{du_1} \frac{\partial u_1}{\partial x} + \frac{y}{u_2} \frac{dp_2}{du_2} \frac{\partial u_2}{\partial x} \right] dx + \left[\frac{x}{u_1} \frac{dp_1}{du_1} \frac{\partial u_1}{\partial y} + \frac{y}{u_2} \frac{dp_2}{du_2} \frac{\partial u_2}{\partial y} \right] dy, \end{aligned}$$

and in order that dP be the derivative of a function,

$$\frac{1}{u_1} \frac{dp_1}{du_1} \frac{\partial u_1}{\partial y} = \frac{1}{u_2} \frac{dp_2}{du_2} \frac{\partial u_2}{\partial x} \quad (5)^\dagger$$

* Footnote on following page.

† It will be noted that under ordinary conditions u_1 , u_2 , $\frac{dp_1}{du_1}$, $\frac{dp_2}{du_2}$ cannot be negative and hence $\frac{\partial u_1}{\partial y}$ and $\frac{\partial u_2}{\partial x}$ or $\frac{\partial p_{1s}}{\partial y}$ and $\frac{\partial p_{2s}}{\partial x}$ must have the same sign or be zero.

If this condition (5) is fulfilled,

$$P_s = \left[\frac{\partial P}{\partial x} \right]_{T, y} = \frac{1}{u_1} \frac{dp_1}{du_1} \left[x \frac{\partial u_1}{\partial x} + y \frac{\partial u_1}{\partial y} \right], \quad (6)$$

* Equation (3) may be obtained directly from the condition for a neutral equilibrium with respect to transformations at constant temperature and pressures, namely

$$F_{12} = F_1 + F_2.$$

For equilibrium to continue to exist for such transformations in the case of variations of the original systems,

$$dF_{12} = dF_1 + dF_2,$$

must hold for such variations, and since $dF = -SdT + vdp$, then at constant temperature these variations must meet the condition,

$$VdP = v_1 dp_1 + v_2 dp_2.$$

However, this treatment does not bring out the fact that dp_1 and dp_2 are to be regarded as capable of independent variation. For example, if

$$F_1 = \frac{n_1 B}{n_1 B + n_2} F_{12},$$

and,

$$F_2 = \frac{n_2}{n_1 B + n_2} F_{12},$$

where B is a constant differing from unity,

then $F_{12} = F_1 + F_2$, but either n_1 and n_2 must be regarded as not independent or F_1 and F_2 and hence p_1 and p_2 must be regarded as not independent. Such a condition of equilibrium would be inconsistent with the requirement that each fluid be independently capable of being in equilibrium with the mixture and that this equilibrium not be disturbed by the addition or removal of the other fluid system. Such conditions for equilibrium may exist in the immediate neighborhood of an interface between fluids where concentration gradients exist; however, these considerations belong properly to the thermodynamics of surfaces, and will not be discussed further here.

Had we considered the equilibrium condition for transformations at constant temperature and volumes, namely,

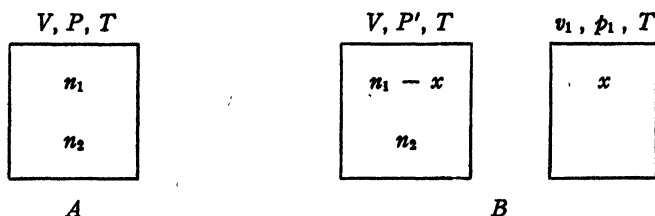
$$A_{12} = A_1 + A_2,$$

we would have arrived at an equation that is essentially similar in physical implications to Equation (3), namely,

$$PdV = p_1 dv_1 + p_2 dv_2. \quad (3a)$$

The physical significance of Equation (3) or (3a) may be illustrated as follows:

Let A and B be two systems at the same temperature which contain the same matter.



We may obtain B by a reversible process from A in any number of ways, e.g., by direct reversible isothermal expansion through a semipermeable membrane, or by decomposing A reversibly into pure n_1 and n_2 then dividing n_1 into $n_1 - x$ and x , then combining $n_1 - x$ and n_2 reversibly in any manner and eventually reversibly expand or compress each separate volume until the system B is obtained. ΔS for the process must be the same in the two processes. Otherwise we could operate a Carnot process in contradiction to the Second Law. Equations (3) and (3a) ensure that ΔS is independent of the path.

The Gibbs equilibrium conditions, $\mu'_1 = \mu_1$, etc., and the derivation of Equation (3) are, of course, very well known and are given in the standard texts. The derivations are repeated here in order to present a reasonably complete picture.

and,

$$P_y = \left[\frac{\partial P}{\partial y} \right]_{v,x} = \frac{1}{u_2} \frac{dp_2}{du_2} \left[x \frac{\partial u_2}{\partial x} + y \frac{\partial u_2}{\partial y} \right];$$

recalling the boundary conditions (Equation 2), $u_1 = x$ when $y = 0$, and $u_2 = y$

when $x = 0$, then $P_y = \frac{dp_2}{du_2} = \frac{dp_2}{dy}$ when $x = 0$, or

$$\int_0^y P_y dy = p_2(u) = p_2(y).$$

The pressure, P , of the mixture will be given by,

$$\begin{aligned} P &= \int_{x=0, y=y}^{x=x, y=y} P_x dx + \int_{x=0, y=0}^{x=0, y=y} P_y dy \\ &= \int_{x=0, y=y}^{x=x, y=y} \frac{1}{u_1} \frac{dp_1}{du_1} \left[x \frac{\partial u_1}{\partial x} + y \frac{\partial u_1}{\partial y} \right] dx + p_2(y). \end{aligned} \quad (7)$$

Thus if we know either u_1 or u_2 as a function of x and y and the equations of state of the two pure fluids, we can determine the equation of state of the mixture. Without a knowledge of u_1 or u_2 as a function of x and y we can tell nothing as regards the equation of state of the mixture.

In order to contrast Dalton's law and the Gibbs-Dalton law, which as we have seen are associated with these problems, we may express these two "laws" mathematically as follows:

Dalton's law,

$$P(x, y) = p_1(x) + p_2(y),$$

Gibbs-Dalton law,

$$P(x, y) = p_1(u_1) + p_2(u_2),$$

that is,

$$P = p_{1e} + p_{2e}.$$

Evidently when $u_1 = x$, and hence $u_2 = y$, the two laws become identical. If we write,

$$\pi_1(x, y) = P(x, y) - p_1(x) - p_2(y),$$

then $\pi_1(x, y)$ is a measure of the departure from Dalton's law, and $\pi_1(x, y)$ is given by,

$$\pi_1(x, y) = \int_{x=0, y=y}^{x=x, y=y} \frac{1}{u_1} \frac{dp_1}{du_1} \left[x \frac{\partial u_1}{\partial x} + y \frac{\partial u_1}{\partial y} \right] dx - p_1(x).$$

While if we write,

$$\pi_2(x, y) = P(x, y) - p_1(u_1) - p_2(u_2),$$

$\pi_2(x, y)$ is a measure of the departure from the Gibbs-Dalton law and $\pi_2(x, y)$ is given by,

$$\pi_2(x, y) = \int_{x=0, y=y}^{x=x, y=y} \frac{1}{u_1} \frac{dp_1}{du_1} \left[x \frac{\partial u_1}{\partial x} + y \frac{\partial u_1}{\partial y} \right] dx - p_1(u_1) - p_2(u_2) + p_2(y).$$

When $u_1 = x$, and $u_2 = y$ for all values of the variables, $\pi_2(x, y) = 0$ and the Gibbs-Dalton law is obeyed, and when the Gibbs-Dalton law is obeyed Dalton's law necessarily holds. However, if $u_1 = xf_1(x, y)$, where $f_1(x, y)$ is homogeneous and of zero degree in x and y , and if each pure gas is ideal, i.e., $p_1 = Ku_1$, $p_2 = Ku_2$, then $\pi_1(x, y) = 0$ and Dalton's law is obeyed but not the Gibbs-Dalton law.

When,

$$P = p_{1e} + p_{2e}.$$

$$dP = dp_{1e} + dp_{2e},$$

but by (4),

$$dP = \frac{v_{1e}}{V} dp_{1e} + \frac{v_{2e}}{V} dp_{2e}$$

$$= \frac{x}{u_1} dp_{1e} + \frac{y}{u_2} dp_{2e},$$

and

$$\frac{v_{1e}}{V} = \frac{x}{u_1} = \frac{v_{2e}}{V} = \frac{y}{u_2} = 1,$$

i.e. $u_1 = x$, $u_2 = y$, and each fluid is as a vacuum to the other fluid regardless of its equation of state. And conversely when each fluid is as a vacuum to the other fluid (that is, $u_1 = x$, $u_2 = y$) then $dP = dp_{1e} + dp_{2e}$ and $P = p_{1e} + p_{2e}$. Evidently this is a highly restrictive condition and can only be regarded as a limiting possible case, rather than as a probable case for physical systems of the type we have been discussing.

It may be pointed out that even when $\frac{x}{u_1}$ and $\frac{y}{u_2}$ are not unity, by superimposing as an experimental condition,

$$dp_{1e} = \frac{(y - u_2)u_1}{u_2(u_1 - x)} dp_{2e},$$

we can find a path along which,

$$dP = dp_{1e} + dp_{2e},$$

and P becomes a function of p_{2e} only. But if $P = p_{1e} + p_{2e}$, in general, where p_{1e} and p_{2e} are independent variables, then,

$$\left(\frac{\partial P}{\partial p_{1e}} \right)_{p_{2e}} = 1 = \frac{x}{u_1},$$

and hence $x = u_1$, $y = u_2$. If, for example,

$$p_{1e} = \phi_1 P,$$

$$p_{2e} = \phi_2 P,$$

and,

$$\phi_1 + \phi_2 = 1,$$

then,

$$u_1 = x, \text{ and } u_2 = y,$$

or there is a functional relation between p_{1e} and p_{2e} (cf. footnote p. 996).

Discussion of Equations and Some Empirical Relations

The various equations presented above, although used to describe what we have called "membrane equilibrium" are in no way dependent on the existence or nonexistence of perfect semipermeable membranes. The treatment has been presented as though the three fluids were contained in three separate, impermeable containers and the equilibrium conditions deduced for variations of a type which would apply physically in the case of ideal membranes. Without reference to some physical process the whole discussion is, of course, practically devoid of meaning. That there are semipermeable membranes which in many cases are fairly close approximations to the ideal semipermeable membrane is unquestionable. When a pure crystalline compound is in equilibrium with a liquid or gaseous solution containing a common component, the interface between the crystalline material and the solution is an example of an almost perfect semipermeable membrane. In fact in many ways, the semipermeable membrane may be regarded as an idealized phase interface. Any mechanism by means of which a *selected* kind of material may be transferred from one volume to another by a reversible process may be regarded as a semipermeable membrane. Depending on the kind of "membrane", it may or may not be capable of supporting a pressure difference between the volumes concerned. The "membrane" must include all parts of systems where concentration or other gradients exist as between the two volumes concerned. The total mass of material in regions where such gradients exist must be small in comparison with the mass of material in the volumes under consideration in order that its variations may be neglected in comparison with the variations of the masses in the volumes concerned. In any case, the thermodynamic equilibrium must not, in any way, be dependent on the properties of the "semipermeable membrane" itself, except in so far as it is or is not capable of supporting a net pressure difference, and a net difference in thermodynamic potentials of selected materials or components. The fundamental condition that the thermodynamic potential of a pure material be the same as that of this material in the mixture or compound substance is the basic condition which virtually defines the semipermeable membrane. From this condition alone we can say practically nothing concerning the temperatures and pressures of the two volumes. However, to parallel real systems in contact with one another, the temperatures obviously must be the

same. While there seems little justification for making any assumptions about the pressures, we shall assume that the pressures are all positive and consider only cases where the pressure of the mixture is not less than the greatest of the equilibrium pressures of all pure systems with which it is in equilibrium.

Equation (5) imposes a considerable restriction on possible simultaneous forms of $f_1(x, y)$ and $f_2(x, y)$ in the equations $u_1 = xf_1(x, y)$, $u_2 = yf_2(x, y)$, although almost any form of either one alone which is consistent with the boundary conditions can be assumed without conflict with thermodynamic principles.

In many practical problems where deviations from the mole fraction law occur it is desirable to have some way of relating the pressures of two-component systems to the pressures of pure components in equilibrium therewith, or to obtain self-consistent relations between concentrations existing across semipermeable membranes in osmotic pressure experiments. In what follows we shall present a few explicit forms of $f_1(x, y)$ and $f_2(x, y)$ which are consistent with various equations of state and may prove useful for extrapolation purposes if not found of interest in themselves.

When $p_1(u_1) = Ku_1$, and $p_2(u_2) = Ku_2$, i.e., when both the pure fluids behave as ideal gases, Equation (5) reduces to,

$$\frac{\partial \log u_1}{\partial y} = \frac{\partial \log u_2}{\partial x},$$

and hence

$$\frac{\partial \log f_1}{\partial y} = \frac{\partial \log f_2}{\partial x}$$

expresses the necessary condition that a thermodynamic equilibrium exist.* If f_1 and f_2 meet this requirement and f_3 and f_4 also meet this requirement,

(i.e., $\frac{\partial \log f_3}{\partial y} = \frac{\partial \log f_4}{\partial x}$), then also,

$$\frac{\partial \log f_1 f_3}{\partial y} = \frac{\partial \log f_2 f_4}{\partial x}. \quad (8)$$

Hence, when individual gases are ideal or nearly so, any products or powers of pairs of explicit solutions of Equation (5) can also form a solution.† If these solutions are homogeneous functions of zero degree in x and y then the equation of state of the gas mixture must also be ideal. Thus,

$$u_1 = x \left(\frac{x+y}{x} \right)^D \cdot \prod_{i=1}^{i=n} \left(\frac{A_i x}{A_i x + B_i y} \right)^{A_i C} \cdot \prod_{j=1}^{j=m} e^{B_j (1-b_j) (y/x)^{b_j}}, \quad (9)$$

$$u_2 = y \left(\frac{x+y}{y} \right)^D \cdot \prod_{i=1}^{i=n} \left(\frac{B_i y}{A_i x + B_i y} \right)^{B_i C} \cdot \prod_{j=1}^{j=m} e^{B_j b_j (x/y)^{1-b_j}},$$

* Cf. the Gibbs-Duhem equation.

† In a purely mathematical sense.

where $A_i \geq 1$, $B_i \geq 1$, $C \geq 0$, $D \leq 1$, $E_i \leq 0$, $0 < b_i < 1$, constitute a general family of possible forms for u_1 and u_2 as functions of x and y , all of which lead to $P = K(x + y)$ and hence to Dalton's law. But of this infinite array of thermodynamically possible forms (it is not intended to imply that these are, by any means, the only such forms) only the special case $u_1 = x$, $u_2 = y$, is also consistent with the Gibbs-Dalton law and the Lewis partial pressure rule.*

The sum of the equilibrium pressures, P_{se} , will be given by,

$$P_{se} = p_{1e} + p_{2e} = p_1(u_1) + p_2(u_2) = Kx \cdot f_1 + Ky \cdot f_2,$$

which is, of course, not in general equal to P but may be greater or less than P .

When $D = 1$, and E and C are zero, in (9)

$$u_1 = x + y = u_2,$$

which corresponds to the case where the fluids are identical, and may be regarded as the limit of applicability of the boundary conditions and definitions. Here

$$P = K(x + y) = p_{1e} = p_{2e}.$$

Other special cases of interest are easily obtained. Thus (9) may be written,

$$\begin{aligned} u_1 &= (x + y) \left(\frac{Bx}{Bx + y} \right)^{BC}, \\ u_2 &= (x + y) \left(\frac{By}{Bx + y} \right)^C. \end{aligned} \quad (10)$$

When x and y are of comparable magnitude and $C = 1$ and $B \rightarrow \infty$ we get the limiting case $u_1 \rightarrow (x + y)e^{-y/x}$, $u_2 \rightarrow 0$ and $P \approx p_{1e} + p_{2e} \approx p_{1e}$, $p_{2e} \rightarrow 0$. Again, when x and y are of comparable magnitude and $B = 1$ and $C \rightarrow \infty$ we get the limiting case $u_1 \rightarrow 0$, $u_2 \rightarrow 0$ and $p_{1e} \rightarrow 0$, $p_{2e} \rightarrow 0$ and $P \gg p_{1e} + p_{2e}$.†

When $f_1(x, y)$, $f_2(x, y)$ are homogeneous functions but are not of zero degrees in x and y , in general Dalton's law will not hold. If the equilibrium conditions are such that,

$$\begin{aligned} u_1 &= x \prod_{i=0}^{i=n} e^{C_i y (xy)^{a_i}}, \\ u_2 &= y \prod_{i=0}^{i=n} e^{C_i x (xy)^{a_i}}, \end{aligned} \quad (11)$$

where $C_i \geq 0$ and $a_0 = 0$, $a_1 = 1$, $a_2 = 2 \dots \dots a_n = n$, and the pure fluids behave as ideal gases,

$$P = K \left[x + y + \sum_{i=0}^{i=n} C_i \frac{(2a_i + 1)}{a_i + 1} (xy)^{a_i + 1} \right].$$

* The Lewis partial pressure rule is assumed to be:

$$p_{1e} = \frac{x}{x + y} P, \text{ or } \mu'_1 = f(T) + RT \log \frac{x}{x + y} P.$$

† Footnote on following page.

† The function f , although somewhat similar to an "activity coefficient" is, of course, by no means identical therewith. It might be regarded as a solubility coefficient at constant potential, the vacuum being taken as unity. When f_1 is greater than unity, x is less than u_1 , i.e., less than it would be if y were zero, and hence y exerts a "negative solvent" action compared to a vacuum. Similarly, when f_1 is less than unity y exerts a "positive solvent" action. Thus taking the simple empirical forms,

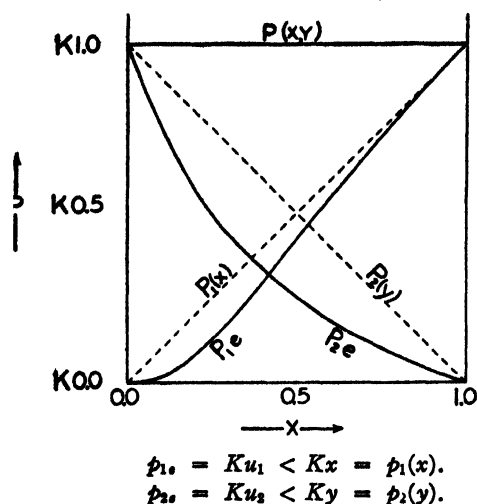
$$f_1 = \frac{x+y}{x} \left(\frac{3x}{3x+y} \right)^a,$$

$$f_2 = \frac{x+y}{y} \left(\frac{y}{3x+y} \right)^b,$$

We have three cases according to the values of a and b . Taking $a = 3$, $b = 1$, as Case I; $a = 1$, $b = 1/3$ as Case II; and $a = 2$, $b = 2/3$ as Case III; we get the following graphs, assuming $x + y = 1$ in each case.

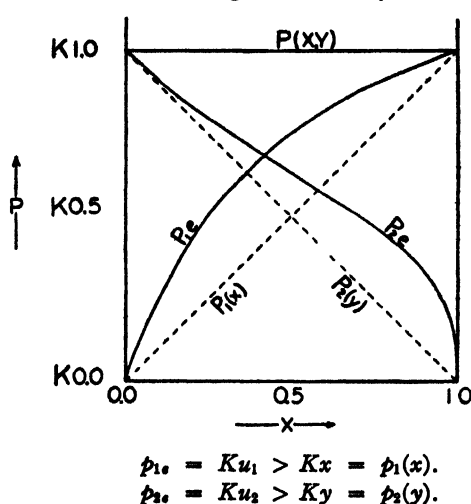
Case I

Positive solubility



Case II

Negative solubility



Case III

Positive and negative solubility

Region a. Positive solubility.

$$p_{1o} = Ku_1 < Kx = p_1(x).$$

$$p_{2o} = Ku_2 < Ky = p_2(y).$$

Region b. Mixed solubility.

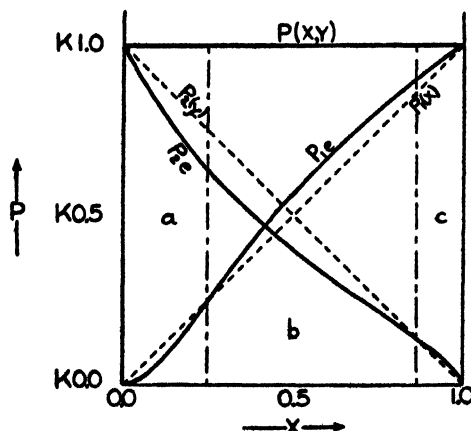
$$p_{1o} = Ku_1 > Kx = p_1(x).$$

$$p_{2o} = Ku_2 < Ky = p_2(y).$$

Region c. Negative solubility.

$$p_{1o} = Ku_1 > Kx = p_1(x).$$

$$p_{2o} = Ku_2 > Ky = p_2(y).$$



It will be noted that $P = K(x + y)$, i.e., that Dalton's law holds in each of the three cases, but the equilibrium pressures are very different from the Lewis partial pressures $\frac{x}{x+y} P$ and $\frac{y}{x+y} P$. (In this case $\frac{x}{x+y} P$ and $\frac{y}{x+y} P$ are identical to $p_1(x)$ and $p_2(y)$, respectively.)

In the special case where $a_0 = 0$ is the only term,

$$u_1 = xe^{Cv}, \quad u_2 = ye^{Cx}$$

and,

$$P = K(x + y + Cxy).$$

Functions of this type (11) yield symmetrical "interaction" terms. Of course there is no need for the "interaction" terms to be symmetrical. Unsymmetrical terms will be given by such expressions as,

$$u_1 = xe^{Cv^2}, \quad u_2 = ye^{2Cvx},$$

and,

$$P = K(x + y + 2Cxy^2).$$

When the pure gases are not ideal, u_1 and u_2 as functions of x and y which are consistent with the condition Equation (5) are much more difficult to find. Moreover, the relation expressed by (8) is no longer valid and we cannot readily obtain general solutions in closed parametric form. However, where observed relations between u_1 and x and y can be approximated by, say, $u_1 = xe^{Cv}$, and where

$$p_1 = Ku_1 + Au_1^2 + Bu_1^3 \dots,$$

$$p_2 = \text{any function of } u_2,$$

then,

$$P = K(1 + Cy)(x + A_1e^{Cvx^2} + B_1e^{2Cvx^3} \dots) + p_2(y).$$

Of course whatever the approximate form of the observed relations, $u_1 = xf_1(x, y)$ or $u_2 = yf_2(x, y)$, $P(x, y)$ as calculated from (7) must be consistent with the observed values for P .

That the Gibbs-Dalton law cannot be considered to apply generally to fluids which are not ideal gases may be illustrated by the following considerations.

Suppose at constant temperature two fluids have the same equations of state, namely,

$$p_1(u_1) = Ku_1 - Au_1^2 + Bu_1^3$$

$$p_2(u_2) = Ku_2 - Au_2^2 + Bu_2^3.$$

If these fluids are *different*, the Gibbs-Dalton law requires that for a mixture of them,

$$\begin{aligned} P &= p_{1s} + p_{2s} = p_1(x) + p_2(y) \\ &= K(x + y) - A(x^2 + y^2) + B(x^3 + y^3). \end{aligned}$$

If, however, the fluids are identical we must have,

$$\begin{aligned} P &= K(x + y) - A(x + y)^2 + B(x + y)^3 \\ &= p_1(x) + p_2(y) + \pi_1(x, y). \end{aligned}$$

In this case $x + y$ represents the total concentration or $x + y = u$. The term $\pi_1(x, y)$ is equal to, $-2Axy + 3Bx^2y + 3Bxy^2$, and may be considerably larger than $p_1(x) + p_2(y)$.

If we hold the composition of the mixture of different fluids constant and vary the total concentration, $x + y$, we may speak of the P, u, T relations of the mixed fluid, u being equal to $x + y$. Evidently the fluid mixture has P, u, T , relations which are quite different from those of either pure fluid. We are thus led to a conclusion which is entirely contrary to experience, namely, that there should be a very marked difference between the P, u, T relations of a given pure fluid and the P, u, T relations of a solution consisting of roughly equal parts of the given fluid and of a second fluid, however small the difference between the two fluids might become.

Evidently the function $f_1(x, y)$ in $u_1 = xf_1(x, y)$ must supply the interaction terms which cannot be lacking in fluid mixtures when the pure fluids are very similar and have nonlinear equations of state.

III. Physical Implications

Equilibrium Pressures; Illustrations

Referring to Fig. 1, when the distributions of the two fluids across the membranes are completely independent so that each fluid acts as a vacuum to each other i.e., when $P = p_{1e} + p_{2e}$, we may decrease the volume v_{1e} , thereby increasing the pressure p_{1e} and the values of u_1 and x by any finite quantity, without altering u_2, y, p_{2e} or v_{2e} . When, however, u_1 is not independent of y , then any finite change in p_{1e} will cause a change in p_{2e} if the volumes V and v_{2e} are kept constant. Thus the system behaves physically, as though the pressure p_{1e} of the pure gas in v_{1e} were partially transferable to the pure gas cell containing the second species. In such cases the pressure in V will be given by $P \geq p_{1e} + p_{2e}$. To illustrate what is involved when the fluids are not independent with respect to the pressures they transmit across the interfaces or semipermeable membranes, and referring again to Fig. 1, let us suppose that the two fluids are in fact independent, so that, $P = p_{1e} + p_{2e}$; and we introduce a third independent fluid into the system. If both membranes are permeable to this third fluid and we represent its equilibrium pressure by p_z , then the new pressure p'_{1e} in v_{1e} will be $p'_{1e} = p_{1e} + p_z$, and similarly $p'_{2e} = p_{2e} + p_z$ and $P' = P + p_z$, where p'_{1e}, P' are the corresponding new pressures in v_{1e} and V , respectively. Now we find that $p'_{1e} + p'_{2e}$ is greater than P' since the added pressure p_z is counted twice in the sum $p'_{1e} + p'_{2e}$. If we had added the third gas only to V , i.e., to the compartment containing the mixture and had assumed the third fluid to be incapable of passing either membrane we would find $p'_{1e} + p'_{2e}$ less than P' . These relations are somewhat analogous to the interaction of fluids which are not independent; if the second component in the mixture can transmit a "force" across the membrane on the pure first component, then the first component in the mixture must exert a force on the second pure component and this will introduce a correction on the additivity

of the equilibrium pressures similar to the case where the ideal fluid passes both diaphragms. On the other hand, the interaction of the two fluids may give rise to other substances, molecular groups or "forces" which cannot pass either diaphragm. In a particular composition these two opposing tendencies might just cancel, and the system at this particular point behave as though independent. As far as real systems are concerned both of these cases should occur quite generally. When the fluids are dilute but react chemically we should expect $P > p_{1e} + p_{2e}$ and where the fluids are fairly concentrated and do not react appreciably, $P < p_{1e} + p_{2e}$. When the fluids are completely insoluble or identical, $P = p_{1e} = p_{2e}$. As an example of the first case, where $P > p_{1e} + p_{2e}$, we might take the case of H_2 and I_2 in equilibrium through semipermeable membranes with HI , H_2 , and I_2 , while as an example of the second case we might suppose the first fluid to be liquid water and the second fluid to be liquid mercury, the diaphragms being permeable to water and mercury respectively. Assuming these liquids completely insoluble in one another, and within the mixed compartment—any water in contact with the water-permeable membrane—any mercury in contact with the mercury-permeable membrane—then the only condition consistent with equilibrium is, $p_{1e} = P = p_{2e}$. In this case p_{1e} must equal p_{2e} and they are completely dependent in the sense that it is not possible to vary one by a finite quantity without varying the other by exactly the same amount as long as the pressures lie within the range of existence of the mutually insoluble liquid phases. In this sense, when the two fluids become identical, again p_{1e} and p_{2e} are completely dependent and $p_{1e} = P = p_{2e}$. But in this case there is no limit to the range of complete dependence, being true at all pressures.

The net pressure across a semipermeable membrane will be $P - p_{1e}$, where the membrane is permeable to the first fluid and p_{1e} is the equilibrium pressure of the first fluid.* In the case of a mixed system in equilibrium with two fluids, $P - p_{1e}$ may be greater or less than p_{2e} according as P is greater or less than $p_{1e} + p_{2e}$. For example, if diaphragm (1) is impermeable to a

* Of course, not, in general, p_{2e} . The common assumption that the net pressure exerted on the diaphragm is p_{2e} can lead to all sorts of absurdities. For example, referring to Fig. 1, assuming the net pressure sustained by diaphragm (1) to be p_{2e} and that sustained by diaphragm (2) to be p_{1e} , then if we move the diaphragms toward one another, thereby tending to separate the fluids in the mixed compartment, we must do work on the system. Since nothing has been said concerning the natures of the diaphragms and fluids, we may suppose the two fluids to be entirely different insoluble liquids, or two liquid phases of different compositions (e.g., water-ether, ether-water solutions) both in equilibrium with the same vapor, or we might suppose the first fluid to be a liquid and the second to be its vapor. We might thus be led to the absurd conclusion that there was a large "entropy of mixing" associated with the removal of a partition separating two fluids already in a state of complete thermodynamic equilibrium. Of course in all of the above cases the net pressures on the fictitious diaphragms are $P - p_{1e} = 0 = P - p_{2e}$. The mere movement of the diaphragms even if accompanied by a definite experimentally identifiable change in distribution of matter does not necessarily involve the performance of work when carried out reversibly.

The validity of such arguments is not so much a matter of the experimental possibility or impossibility of separating mixtures by means of such membranes, but is rather a question as to whether such "separations" conform analytically to the idealizations implied in the mathematical operations, $(\frac{\partial A_{12}}{\partial n_1})_{T,V,n_2}$, $(\frac{\partial A_1}{\partial n_1})_{T,V,n_2}$, etc. These operations include the case where n_1' and n_2' are arbitrary divisions of a single variable n , i.e., the case of identical fluids.

liquid but permeable to its vapor, it is possible for a net pressure to exist across the diaphragm (not, perhaps, strictly a condition of absolute physical stability). Let the net pressure be p_z , then $p_z = P - p'_1$, where p'_1 is the vapor pressure of the liquid under these conditions. Now p_z might be a pressure due to an insoluble inert gas on the liquid side of the diaphragm (1). If the gas acts as a vacuum to the vapor of the liquid and p_{2e} is the equilibrium pressure of this inert gas, then $p_z = p_{2e}$, since $P = p_z + p'_1 = p_{2e} + p'_1$. But if the vapor and inert gas are not mutually independent $p_z \geq p_{2e}$ and the net pressure across diaphragm (2) is $P - p_{2e} = p'_1 + p_z - p_{2e} \geq p'_1$.

If the "membrane" cannot support a net pressure toward the mixture, as might be the case when the "membrane's" only function is to prevent passage of part of the mixture toward the pure fluid, then P cannot be less than the greater of p_1 and p_2 , and, hence, the smallest value of $P/(p_1 + p_2)$ is one-half, while the greatest value is unlimited. However, using the expression "membrane equilibrium" in its most general sense P might be less than either one of p_1 and p_2 . In any case, there is certainly no thermodynamic justification, whatever, for the assumption that $p_1 = P - p_2$.

Thermodynamic Quantities

As we have pointed out in the first part of this paper the expression "the entropy of mixing" is usually used to denote the entropy change associated with the combining of two separate volumes of fluids into a single fluid mixture whose volume is equal to the sum of the original volumes. Let us, rather, consider the changes, if any, in the thermodynamic quantities associated with the converting isothermally of n_1 moles of the first kind of fluid and n_2 moles of the second kind when each alone is contained within a volume V , into a mixture containing the same matter in an equal volume V .

In order to combine the gases reversibly we must first expand or compress each gas separately until each separate gas is in such a state as to be in thermodynamic equilibrium with the mixture to be formed. Then the two gases are to be combined reversibly, the two volumes disappearing isothermally under their respective equilibrium pressures p_1 , p_2 , while a single volume of mixture under its equilibrium pressure P makes its appearance.

The total heat received will consist of two parts. First there will be the heat received in bringing each fluid to its equilibrium state, namely,

$$T\Delta S_1 = \int_V^{v_1} dE_1 + \int_V^{v_1} p_1 dv_1 + \int_V^{v_2} dE_2 + \int_V^{v_2} p_2 dv_2.$$

Second, there will be the heat absorbed in the equilibrium conversion, namely,

$$T\Delta S_2 = E_{12} - (E_1 + E_2) + PV - (p_1 v_1 + p_2 v_2).$$

While the observed value of the total heat received in the two processes divided by the temperature would measure the total entropy change, $S_{12} - (S_1 + S_2)$, the equations of state in terms of P , u , and T will not enable us to

calculate the entropy change even if we know the equilibrium conditions, since we must also know the absolute value of the energies* as functions of the volumes for the pure fluids as well as for the mixture.

When $u_1 = x$, $u_2 = y$, represent the equilibrium conditions then, as shown by Gibbs, all of the thermodynamic quantities are additive and $T\Delta S_1 = T\Delta S_2 = 0$, regardless of the equations of state of the individual fluids.

When each pure gas, as well as the mixture, is ideal in the sense that $pv = nRT$ and $E = 3/2 nRT$, then $T\Delta S_2 = 0$, regardless of whether $u_1 = x$, $u_2 = y$, or not. However, $T\Delta S_1$ will not be zero when u_1 and u_2 are not equal to x and y respectively. When both gases are ideal and the equilibrium conditions require equal concentrations on either side of the semipermeable membranes then $\Delta S = 0$ for the entire process of combining equal volumes into a single equal volume. Each gas is then behaving as a vacuum to the other gas. We should contrast this limiting case of completely independent ideal gas mixtures with the limiting case of completely dependent ideal gas mixtures. In the latter case $p_{1e} = P = p_{2e}$ and the only condition consistent with this is $u_1 = x + y = u_2$, and since this implies that $n_1 = n_2$, ΔS becomes equal to $-R \log 2$ per mole.

The entropy change which accompanies the removal of a partition between two fluids, having the same pressure and temperature, is to be obtained in the same way except that in place of the lower limit V in the first integration we use V_1 and V_2 respectively, V_1 and V_2 corresponding to the initial fluid volumes and $V_1 + V_2 = V$. Where E and (PV) are constant, as would be the case for ideal gases whose mixtures obey Dalton's law and where $E_{12} = E_{1e} + E_{2e}$, the entropy of mixing will be given by,

$$\Delta S = RV \left[x \log \frac{x+y}{u_1} + y \log \frac{x+y}{u_2} \right],$$

where u_1 and u_2 must be homogeneous functions of first degree in x and y . Putting in the values of u_1 and u_2 from, say, (10) we get,

$$\Delta S = RV \left[x \log \left(\frac{Bx+y}{Bx} \right)^{Bc} + y \log \left(\frac{Bx+y}{y} \right)^c \right].$$

When the equilibrium pressures are completely "dependent", as would be the case were the fluids identical, $C = 0$ and the entropy of mixing vanishes, as it should. When the equilibrium pressures are completely independent, then $B = C = 1$, and we get the classical entropy of mixing. When x and y are of comparable magnitude and either B or C are large we get large values for the entropy of mixing. Thus comparing the entropy of mixing associated with the removal of the partition, in the limiting cases of (a) complete "dependence" of pressures, (b) complete independence, and (c) the limiting

* In other words we must know ΔE for the process. When dealing with mechanical model gases we usually assume absolute energies although such absolute energies have little or no meaning thermodynamically (cf. footnote, p. 1009).

cases where B or C approach infinity, we have (a) no entropy change, (b) an entropy change corresponding to $R\mathcal{V}\left[x \log \frac{x+y}{x} + y \log \frac{x+y}{y}\right]$, (c) an infinite entropy change.

Real fluids may be expected to show an entropy of mixing varying between these limits. Of the three limiting cases, evidently, the first is the suitable choice of limiting condition from which real systems may be expected to deviate as the fluids become physically distinguishable from one another, since this condition must hold for identical fluids and may be closely approached in many cases when fluids are either very similar or insoluble. In any case, it is evident that by introducing the equilibrium condition, which is absolutely essential to any calculation of the entropy of mixing, we avoid a good many of the difficulties of the Gibbs Paradox.

It is to be emphasized that the relations we have put forward in Part II of this paper apply without any reservations concerning the energies of the gases involved, and apply to cases where ΔE is zero for the mixing process as well as to cases where ΔE is not zero. Consequently when Dalton's law is obeyed and the gases are all ideal, ΔH for the mixing process may have almost any value. The relations of Equation (9) are thus perfectly applicable to cases where ΔH is zero as well as to cases where ΔH is not zero.

When two dilute diatomic gases A_2 and B_2 , each of which obeys Boyle's law closely, react to form the gas AB , which also obeys Boyle's law, we might have an example of a case when p_{1e} and p_{2e} were small compared with P , while Dalton's law was obeyed. Depending on the relative values of the bond energies $A-A$, $B-B$, and $A-B$, such reactions may or may not be associated with a large ΔE and hence a large ΔH . While large negative values of ΔF are usually associated with large negative values of ΔH , $(-\Delta F)$ may be quite large when ΔH is practically zero. In such cases there is a large positive entropy change accompanying the reaction. Thus ΔE and ΔH might be zero for such a reaction as $A_2 + B_2 = 2AB$, while $p_{1e} \ll P$ and $p_{2e} \ll P$, and there will be a large entropy of "mixing" or "reaction". It is also perfectly permissible thermodynamically that $p_{1e} \approx P$ and $p_{2e} \ll P$, when ΔE and ΔH are zero, but these relations are difficult to interpret in terms of any sort of ordinary chemical reaction. Such relations seem to imply that it is possible for the relative capacities for thermal energy of constituents to change on mixing. Cases where $p_{1e} > p_1(x)$, $p_{2e} < p_2(y)$ should be observable in the case of ideal gas mixtures but can hardly be due to any ordinary chemical reaction.

When surface forces are not excluded the situation may be quite different. Thus, if in a real gas mixture, the value of $(-\Delta F)$ for the reaction of each gas alone with the wall of the container is large in comparison with $(-\Delta F)$ for the reaction of the gases themselves, and the rate of exchange of energy of each gas with the wall is large in comparison with the rate of exchange of energy between the gases themselves, then each gas can be more or less independently in a state of equilibrium with the wall. In the limiting case, each

gas can act as a vacuum to the other gas. Even identical gases may show an entropy of mixing, under such extreme circumstances, owing to a change in surface volume ratio. Such a situation might prevail in a very dilute gas mixture contained within a comparatively small volume, where the mean "free path" of the gas molecules was large in comparison with the dimensions of the container. Under these circumstances the whole gas is dominated by the wall reaction equilibrium and the free energies, energies, entropies of the fluid are by no means small compared to surface free energies, etc. For more concentrated systems such a condition might prevail in the immediate neighborhood of the surface.

When p_{1s} and p_{2s} are independent, in the sense which we have been using, the other thermodynamic properties are also independent and in such cases we may speak of the energy, entropy, etc., of a constituent of a mixture. Although even in this case the total work which can be done in an adiabatic expansion through a semipermeable membrane is equal to the whole of the thermal energy of the mixture, and hence we might regard the energies of each component as being the same, assuming all of the energy to be thermal energy. When, however, p_{1s} and p_{2s} are not independent the other thermodynamic properties are not independent and the assigning of energies, entropies, etc., to components within a mixture becomes highly arbitrary. Such relations as those of Equation (10) indicate that even in the case of an ideal gas mixture where $PV = (n_1 + n_2)RT$ and $E = (n_1 + n_2)3/2RT$ and where $n_1 = n_2$ the thermodynamic potentials of each component may be very different.* When such a difference exists it seems inescapable that if there is to be any meaning to the notion of the free energy per mole of a constituent within a mixture, then these free energies must differ. While we might similarly suppose, in such cases, that the energies per mole must also differ, it must be borne in mind that we might equally well suppose that the mean energies were the same but that the entropies differed. Evidently such distinctions have an arbitrary character from a thermodynamic point of view. If we regard all of the energy as kinetic energy of translation it is evident that there is no purely thermodynamic requirement that mean kinetic energies of different kinds of gas molecules in gas mixtures shall be the same. In fact the limiting case of Equation (10) where B approaches infinity, and $C = 1$, would indicate that thermodynamically it would be perfectly possible that one kind of gas have practically all of the kinetic energy, while the second kind have practically none, even when the molecules of each were equally numerous. The fact that such a partition of kinetic energy makes the entropy of the mixture a maximum and thus in a certain sense "most probable" is no justification for ignoring the physical constraints necessarily present in real gas mixtures and thus concluding that real gas mixtures which approximate the ideal gas laws will behave in any such manner. It does indicate, however, that such limiting cases are thermodynamically possible and that, depending on the detailed

* Strictly, comparisons of thermodynamic properties of fluids are meaningless unless the fluids are convertible into one another reversibly. Here it is assumed that the pure gases have the same potentials when having the same T and P .

physical nature of the gases, it is quite possible thermodynamically for real gases which obey the ideal gas laws and Dalton's law, to show an entropy of mixing varying from zero to large values, even when $\Delta H \approx 0$ for the process.

If we wish a detailed mechanical "explanation" or model of such thermodynamic relations, obviously we must seek such a model outside of the field of thermodynamics and consequently such discussions do not belong here. However, it may not be out of place to mention briefly one or two points that have some slight bearing on such problems.

It will be immediately evident that if we suppose that all of the energy of every ideal gas is wholly kinetic energy of translation and that at a given temperature every such pure gas has a Maxwellian distribution of velocities about a modulus proportional to the temperature, and every constituent of a gas mixture has the same velocity distribution, the constituent gas and pure gas are identical and hence each such gas is as a vacuum to every other such gas. If, however, we only require that the energy distribution of the whole gas mixture be Maxwellian and permit constituent gases to have non-Maxwellian velocity distributions, relations such as those of Equation (10) where $B > 1$, $C = 1$, would not be excluded. In this case the forms of the velocity distributions of the constituent gases could hardly be consistent with statistical independence of velocity components. In any case it is evident that there is no purely thermodynamic requirement that each constituent in a gas mixture have a Maxwellian distribution of velocities when the whole gas has its energy distributed canonically or is Maxwellian with respect to its kinetic energy.

Metastable Equilibrium and Boundary Conditions

When we write the condition for equilibria, as regards distribution of material across a semipermeable membrane in the form,

$$u_1 = x \cdot f(x, y) \quad \text{or} \quad u_1 = (x + y)f'(x, y),$$

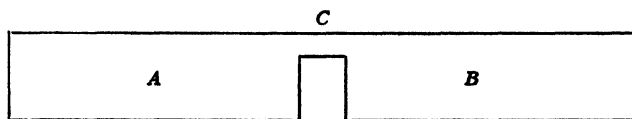
and suppose that $u_1 = x$ when $y = 0$ is a necessary condition which we can impose as a boundary condition on $f(x, y)$ we are assuming that we are not in a range of values where u_1 itself is indeterminate. Writing the equation of state in the form,

$$P = P(u),$$

at constant temperature, there may be not more than three values of u consistent with a given pressure and temperature. Since there may be any quantity of each phase the value of u within a container containing more than one phase is indeterminate as far as equilibrium conditions are concerned. When the temperature is such that there may be two values of u consistent with a given pressure P_* , as we increase the value of u , P will increase until the pressure P_* is reached after which (if the second phase is present in small but finite quantities) the value of u may be increased by a large factor—a thousandfold or more in many cases—and P_* will remain constant. (In the complete absence of the second phase the pressure will normally continue

to increase smoothly and undergo no distinctive change in the neighborhood of the point P_c .) Thus μ may be not completely defined in terms of P and T in such regions.

As far as membrane equilibrium is concerned, (i.e., equilibrium with respect to the distribution of mass between volumes) when T and P have such values that two or more states may coexist, the distribution of matter across a permeable membrane or across an imaginary plane becomes essentially indeterminate. In this region infinitesimal forces or purely passive resistances may permanently stabilize one state as compared with another. The indeterminate character of such systems may be simply illustrated as follows:



Let A and B represent two large shallow closed vessels connected by means of a narrow passage C , the whole being immersed in a thermostat. If initially we place solid tungsten, copper, or liquid mercury in B and assume that A contains the corresponding vapor at the equilibrium pressure, a comparatively permanent state will exist where the concentration of material in B is vastly greater than in A , even when very considerable adventitious variations in temperature and external fields occur. The distribution of mass will be the more nearly perfectly stationary, the larger the passive resistances and the smaller the variations in the external influences. If, however, we had placed liquid water in B and water vapor, at the equilibrium pressure, in A , the permanency of the unequal mass distribution will be largely determined by external circumstances, the distribution tending to equalize rapidly if there are fairly large temperature variations as between A and B where such variations produce no net tendency toward an unequal distribution. A comparatively permanent unequal distribution would result from a number of small influences, such as a trace of soluble material in one compartment, a gravitational field in the direction of $A \rightarrow B$, a minute net temperature difference, etc. If completely shielded from all outside influences, it would require a great length of time to achieve complete equality of density in the two vessels. While these systems may, perhaps, be regarded as not "stable" in a statistical sense but only "metastable" they are essentially cases of indeterminate equilibria and exhibit a number of properties characteristic of these regions. In such regions the observed distribution of material will be determined by the magnitude of the passive resistances to change in comparison with the magnitudes of the adventitious variations in external forces. When the passive resistances are small the behavior will be characteristic of the external conditions, (e.g., the nature of the variations of the "temperature" of the thermostat, the gravitational effects, etc.) rather than characteristic of the material itself. These conditions would prevail at the "critical temperature". Here the uncertainty in density distribution would not be as great as would be the

case at temperatures below the critical temperature, but the sensitivity of the system to external agencies would be greater, the passive resistances being, in general, less. In none of these cases is the distribution of matter a characteristic of the thermodynamic equilibrium. Thermodynamically the dense and attenuated phases, while not identical, are identical with respect to any tendency toward change (their values of E and S per unit mass are not the same, but their values of $E - TS$ per unit mass are the same) as are all mixtures thereof, which do not introduce appreciable surface free energies. Thermodynamically the concentrations are not defined in such regions. Any processes which tend to change the distribution of matter as between the two vessels when in a state of thermodynamic equilibrium are not finite thermodynamic processes since no finite ΔS , ΔE , ΔF , etc., can be assigned to them.

Returning to the membrane equilibrium equation,

$$u_1 = x \cdot f_1(x, y),$$

not only will this relation not be defined when there can be more than one value for u consistent with a given value of p_1 , and T , but the mixture containing x and y may also be capable of other values. A given mixture (x, y) may have such values of P and T that a second system (x', y') , where x' and y' are much greater than x and y , respectively, is capable of coexistence with the less dense mixture (x, y) and hence with u_1 .

We can apply Equation (7) if we know the complete equations of state $p_1(u_1)$, $p_2(u_2)$, and u_1 as a function of x and y for all values for the variables. But generally we do not know these equations completely. However, if we specify that u_1 , u_2 , x , and y always refer to the smallest densities consistent with given values of p_1 , p_2 , and T , we can retain the boundary conditions, $u_1 = x$ when $y = 0$, and $u_1 = 0$ when $x = 0$, as well as using approximate equations of state and an approximate relation $u_1 = x \cdot f_1(x, y)$, all of which shall be of reasonable validity for the small values of x and y and so obtain P as a function of x and y which is also of reasonable validity.

While these boundary conditions have been discussed with relation to semipermeable membranes, they are not primarily dependent on such membranes but are related to what is inferred in the whole structure of thermodynamics, namely, that an equation of state is applicable to bodies of matter and that an equation of continuity is applicable to thermodynamic processes. The first assumption regarding the equation of state may be put in many forms, one of which is that if two bodies consist of the same mass and of the same kind of matter, and each body is under the identical external forces (temperature, pressure, e.m.f., etc.), and if each body occupies the greatest volume consistent with its being in a state of reversible equilibrium with these forces, the volumes will be the same, the energies, entropies, etc., will be the same. Similarly, if the volumes are the same, the external conditions the same, and each contains the same kind of matter and the smallest mass consistent with its being in a condition of reversible equilibrium with its environment, the masses, etc., will be the same. Again, if each have the greatest entropy consistent with its

volume, mass, etc., the energies, etc., will be the same. The second underlying assumption is that if one of the bodies contain an infinitesimal mass of another kind of material which when pure has a finite density, energy, etc., under the given external conditions, the greatest volumes of the two masses, one pure and one impure, consistent with their being in a state of reversible equilibrium with the external conditions, cannot differ by more than an infinitesimal, the energies, entropies, etc., cannot vary by more than an infinitesimal. The differences must approach zero continuously as the quantity of the impurity approaches zero. Thus to each body of matter an equation of state of the form

$$\phi(T, P, X, V, M, \mu_1, \mu_2, \dots) = 0$$

is applicable, where T is the temperature, P the pressure, X other external forces, V the volume, M the mass and μ_1, μ_2 , etc., are the thermodynamic potentials of each kind of matter comprising the whole mass M .

IV. Concluding Remarks

It is obvious that ordinary liquids do not obey the Gibbs-Dalton law even approximately. It is equally obvious that gases which obey Boyle's law very closely but which react chemically do not obey this law. Gillespie (2), McHaffie (3), and others have shown that the Gibbs-Dalton law does not hold for such gas mixtures as $H_2 + NH_3$, $N_2 - NH_3$, $H_2O - \text{air}$, etc., the concentration of H_2O or NH_3 being as much as 50% higher and in some cases appreciably lower than required by the Gibbs-Dalton law. The classical experiments of Dalton, Reguault, and Magnus are to be regarded as approximate verifications of Dalton's law, not the Gibbs-Dalton law. As far as we are aware, very few experiments have been carried out in order to ascertain whether the Gibbs-Dalton law holds in regions where the gases are reasonably close approximations to ideal gases which do not react chemically in the ordinary sense. These regions are, by far, the most interesting regions in which to test the validity of the Gibbs-Dalton law. If appreciable deviations were found in cases of nearly ideal inert gas mixtures it would permit the various contributing factors to be correlated much more readily than would be the case were the gases not nearly ideal, and thus might lead to the discovery of some hitherto unknown general relations.

While we have perhaps overemphasized the fact that the Gibbs-Dalton law is not generally valid and, without considerable qualifications has neither a theoretical nor an experimental basis, Gillespie seems to have interpreted Gibbs' statements in this connection as implying that the law is generally applicable to fluid mixtures. It is our opinion that Gibbs meant this law as generally valid only in the case of mixtures of perfect inert gases. When so restricted the law is in conformity with classical kinetic theory, i.e., to what is usually assumed concerning the mixing of Maxwellian gases, as well as being in conformity with the usual application of modern statistics to such problems. However, it must be pointed out that the Maxwellian gas, the Einstein-Bose gas, the Fermi-Dirac gas, etc., are all model thermodynamic

fluids, and, in so far as the theoretical treatment of mixtures of these model fluids which obey Dalton's law exactly, requires the Gibbs-Dalton law to be obeyed, the theoretical treatment goes beyond thermodynamic requirements, and hence beyond the thermodynamics the models are intended to illustrate. While such theoretical treatment may often be valid, it is our opinion that it is too restrictive and should not be regarded as generally valid without a great deal more experimental evidence. It is thought that many cases can be found where real gas mixtures obey Dalton's law quite closely and where the energies are additive but the entropies not additive. Moreover, it is thought that among those cases where the thermodynamic potentials of the constituents are changed as a result of the mixing, there will be cases where the thermodynamic potential of one constituent is increased while that of the other constituent is decreased, as well as the more generally recognized case of "chemical" reaction, where both thermodynamic potentials are decreased. In other words, when Dalton's law is obeyed it is quite possible thermodynamically that the equilibrium pressure of a given constituent gas may be greater than the pressure which the same gas would exert if it occupied the space alone. Accordingly such cases should be observable. However, there may be reasons apart from thermodynamics why such cases cannot occur.

If it is, indeed, a general experimental fact that deviations from the Gibbs-Dalton law are always negligible when deviations from Dalton's law are negligible, and where there is no evidence of chemical reaction, in the ordinary sense, then Dalton was essentially right in stating that different gases act as a vacuum to one another. If, however, this is not generally true, as what little experimental evidence there is seems to indicate, then the paradox concerning the entropy of mixing is largely an illusion, and theoretical treatments of statistical model mixtures which assume that the statistics of constituents in mixtures are mutually independent are not necessarily valid even in cases where each pure constituent gas is ideal as well as the gas mixture.

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ERRATA

Page 258, Reaction (1), for " CO^{80+++} " read " Co^{80+++} ".

Page 561, Table II, second row of figures:

Column 1, for 0.697 read 0.692

Column 3, for 1.257 read 1.276

Column 4, for 1.62 read 1.64

Page 877. Reference (6). For "Phys. Rev. 69 : 243. 1946" read "Phys. Rev. 70 : 568. 1946".

Reference (8). For "Phys. Rev. 70 : 92. 1946" read "Phys. Rev. 69 : 243. 1946".

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